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NAME OF AUTHOR/*NOM DE L'AUTEUR* Johannes G.A.A.M. Reuvers

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SYNTHESIS AND STEREOCHEMICAL NONRIGIDITY OF COMPLEXES DERIVED FROM $[(C_7H_7)Fe(CO)_3]^-$.

by

© JOHANNES GERHARDUS ANTONIUS ANDREAS MARIA REUVERS

A THESIS
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled SYNTHESIS AND STEREOCHEMICAL NONRIGIDITY OF COMPLEXES DERIVED FROM $[(C_7H_7)Fe(CO)_3]^-$ submitted by Johannes G. Reuvers in partial fulfilment of the requirements for the degree of Doctor of Philosphy in Chemistry.

Josef Takats.

Josef Takats, Supervisor

Julio Desparello

W.A.G. Graham

D. Rankin

John Hoz

Martin Cowie

Date April 9. 1979

Aan mijn ouders

ABSTRACT

The reactivity of the anion $[(C_7H_7)Fe(CO)_3]^-$ has proven it to be a versatile precursor of fluxional organometallic complexes.

The different reaction patterns observed in the interaction of $[(C_7H_7)Fe(CO)_3]^-$ with main group IV electrophiles demonstrates the synthetic utility of this anion. The reaction of the anion with R_3MX, R = CH_3, M = Si, Ge, and R = C_6H_5, M = Ge, and X = halide, yielded the ring substituted compounds (*exo*-7-$R_3MC_7H_7$)$Fe(CO)_3$. The synthesis and characteristic properties of the compounds are described. Variable temperature proton and carbon-13 NMR spectra showed that these complexes are fluxional. The mechanism of the process responsible for the temperature dependent NMR spectra was identified as an oscillatory motion of the $Fe(CO)_3$ moiety with respect to the C_7H_7 ring, corresponding to an *apparent* 1,3 iron shift. A norcaradienetricarbonyliron species is considered as a possible intermediate in the rearrangement, implying the operation of two sequential 1,2 shifts for the iron migration. The free energy of activation obtained for the complex $(7-(C_6H_5)_3GeC_7H_7)Fe(CO)_3$ by the spin saturation transfer (Forsén-Hoffman) NMR technique (77 kJ mol^{-1}) agrees well with that extracted by conventional line shape analysis (73 kJ mol^{-1}, $T_c \simeq 120°C$).

In contrast the reactions of $[(C_7H_7)Fe(CO)_3]^-$ with $(C_6H_5)_3MCl$, M = Sn and Pb, resulted in η^3-coordinated cycloheptatrienyltricarbonyliron complexes. The observation of a sharp singlet for the C_7H_7 resonance in the ^1H and ^{13}C NMR spectra of these compounds at ambient temperature indicated the fluxional nature of the complexes. Variable temperature NMR spectra established the η^3-coordination of the C_7H_7 ring while the observed line shape changes clearly indicated the 1,2-shift as the operative mechanism. The reactivity of $(\eta^3\text{-}C_7H_7)Fe(CO)_3Sn(C_6H_5)_3$ is commented upon.

The reactivity of $[(C_7H_7)Fe(CO)_3]^-$ towards other main group and transition metal electrophiles has also been studied and is discussed.

Attempts to synthesize the compound trans-μ-(1-4-η:5-7-η-C_7H_7)$Fe(CO)_3Fe(CO)_3Sn(C_6H_5)_3$ failed, instead a cis-dinuclear complex was identified and $(\eta^5\text{-}C_7H_7)Fe(CO)_2Sn(C_6H_5)_3$ could be isolated. Two distinct temperature dependent processes are operative in this compound. The coalescence temperature for the high-energy process, which equilibrates *all* hydrogen positions of the seven-membered ring, is considerably higher than the T_c for the corresponding process in the case of $(\eta^3\text{-}C_7H_7)$-$Fe(CO)_3Sn(C_6H_5)_3$ (+30°C versus -60°C for $(\eta^3\text{-}C_7H_7)Fe(CO)_3$-$Sn(C_6H_5)_3$). The mechanisms of both the high- and the low-temperature process observed for $(\eta^5\text{-}C_7H_7)Fe(CO)_2Sn(C_6H_5)_3$ are delineated.

The complex $(7\text{-}(C_6H_5)_3GeC_7H_7)Fe(CO)_3$ could be *endo*-deprotonated, this is in contrast to the parent molecule where only *exo*-proton abstraction is observed. The resulting anion $[((C_6H_5)_3GeC_7H_6)Fe(CO)_3]^-$ could be deuterated to yield exclusively two isomers, $(3\text{-}(C_6H_5)_3Ge,7\text{-}DC_7H_6)Fe(CO)_3$ and $(6\text{-}(C_6H_5)_3Ge,7\text{-}DC_7H_6)Fe(CO)_3$. The isomers could be separated by repeated fractional crystallization. Deuteration of these two complexes showed that electrophilic addition to the seven-membered ring occurs stereo- and regioselectively, i.e., *exo* attack at the *uncoordinated* double bond is observed.

The regioselectivity of the electrophilic deuteration of $[((C_6H_5)_3GeC_7H_6)Fe(CO)_3]^-$ is discussed in view of the data available on its low temperature limiting ^{1}H NMR spectrum and with respect to the recently formulated rules concerning nucleophilic addition to coordinated unsaturated hydrocarbon ligands in cationic organometallic complexes. The reactivity of this anion towards main group IV electrophiles is commented upon.

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Abbreviations

Me	- methyl, CH_3
Et	- ethyl, C_2H_5
Ph	- phenyl, C_6H_5
t-Bu	- tertiary butyl, C_4H_9
n-Bu	- n-butyl, C_4H_9
Cp	- η^5-cyclopentadienyl, C_5H_5
Ac	- acetyl, $H_3CC(O)$
pz	- pyrazolyl, $C_3N_2H_3$
py	- pyridine, C_5H_5N
PPN^+	- bis(triphenylphosphine)iminium, $(Ph_3P)_2N^+$
TCNE	- tetracyanoethylene, $(NC)_2CC(CN)_2$
THF	- tetrahydrofuran, C_4H_8O
TMS	- tetramethylsilane, $(CH_3)_4Si$
TFA	- trifluoroacetic acid, CF_3COOH
BDA	- benzylideneacetone, trans-4-phenyl-3-buten-2-one, $PhCHCHC(O)CH_3$

CHAPTER ONE

INTRODUCTION. TRANSITION METAL ORGANOMETALLIC COMPLEXES OF THE CYCLOHEPTATRIENE AND CYCLOHEPTATRIENYL LIGANDS.

1. The coordination of unsaturated hydrocarbons to transition metals. Bonding in polyene-metal complexes.

The nature of the bonding in cyclic and acyclic polyene-metal complexes has been studied extensively and several reviews have appeared.[1] While we will consider a detailed molecular orbital description of the bonding in $[(C_7H_7)Fe(CO)_3]^-$ below, it suffices here to recall a simplified qualitative picture of the interaction between the polyene and the metal center.[2] Upon coordination of the polyene, overlap of the highest occupied molecular orbital (HOMO) of the polyene with (an) empty metal orbital(s) of suitable symmetry (and mainly d-orbital in character) occurs, resulting in a donation of electron density from the ligand to the metal. Overlap of (a) filled metal orbital(s) with the lowest unoccupied molecular orbital (LUMO) of the polyene (which is often antibonding with respect to the polyene C=C double bonds) results in the donation of electron density to the organic ligand. The two contributions to the bonding are synergic in character and are comparable to the effect on the polyene of exciting an electron from the HOMO to the LUMO.[2] An equalization of the C-C bond lengths in the bound fragment of the polyene is expected from either bonding contribution. In addition it is also anticipated that the reactivity of the bound organic moiety will be rather different than that of the free ligand. For example, upon coordination to the $Fe(CO)_3$ moiety the anti-aromatic ligands cyclobutadiene and cyclooctatetraene exhibit chemical and geometric properties characteristic of an aromatic hydrocarbon: equalization of the carbon-carbon bond lengths,[3,8,9] a tendency to undergo electrophilic substitution,[3,5,7] and a lack of reactivity towards $(4\pi + 2\pi)$ Diels-Alder reagents.[6] The last two characteristics are particularly apparent for the cyclobutadiene ligand in $(\eta\text{-}C_4H_4)Fe(CO)_3$.[7] The crystal structure of a substituted derivative of the latter compound has been reported.[8] The dihedral geometry of $(\eta^4\text{-}C_8H_8)Fe(CO)_3$ is shown below;[9] note the equal C(1)-C(2), C(2)-C(3), and C(3)-C(4) bond distances.

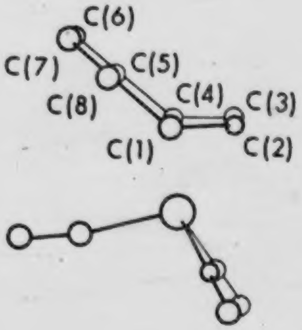


Figure I. The structure of $(C_8H_8)Fe(CO)_3$.[9] Bond distances are C(1)-C(2) = C(3)-C(4) = 1.42, C(2)-C(3) = 1.42, C(4)-C(5) = C(1)-C(8) = 1.45, C(5)-C(6) = C(7)-C(8) = 1.34, and C(6)-C(7) = 1.49 (all ± 0.02 Å).

The geometries and reactivities of non-cyclic polyenes follow an identical pattern.[3] For example, this is illustrated by the solid state structure of (η^4-butadiene)-$Fe(CO)_3$[10] in which the observed C-C separations, 1.46 Å, in the diene moiety are identical within experimental error. The above characteristics are also particularly well exhibited by the tricarbonyliron complex of 2-vinylnaphtalene,[11] Figure 11.

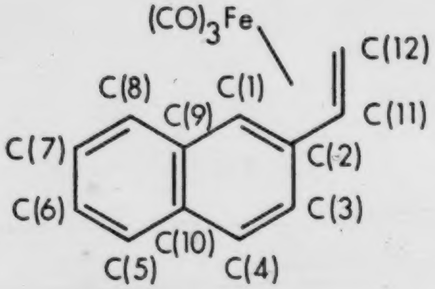
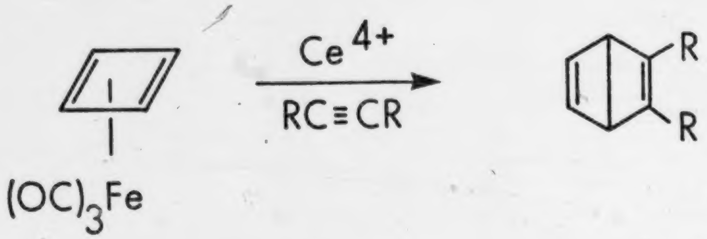


Figure II. The structure of the $Fe(CO)_3$ complex of 2-vinylnaphtalene.[11] Selected bond distances are: C(1)-C(2) = C(2)-C(11) = C(11)-C(12) = 1.41 Å, C(2)-C(3) = C(4)-C(10) = C(9)-C(1) = 1.46 Å, and C(3)-C(4) = 1.31 Å.

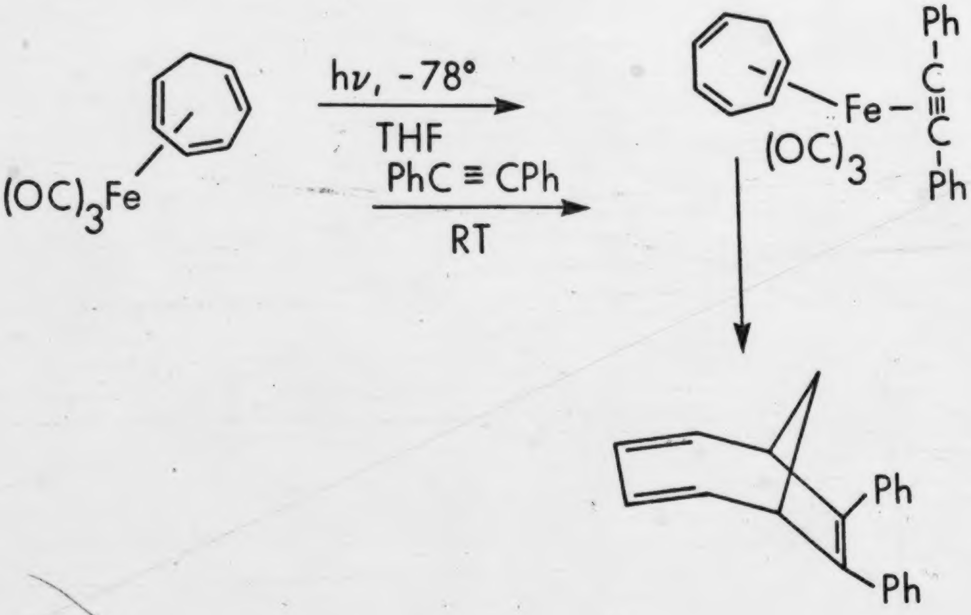
Transition metal complexes find particular application in the stabilization of otherwise highly reactive organic substrates. Examples are found in the tricarbonyliron complexes of cyclobutadiene,[7,12] trimethylenemethane,[13] pentalene[14] and tricyclo(4.4.0.$0^{2,5}$)deca-7,9-diene.[15]

Often the reactive organic species can be generated *in situ* by removal of the transition metal fragment and subsequently be used in the synthesis of new organic molecules, equation (1).[16]



(1)

Transition metals can thus be used in the stabilization of otherwise unstable molecules and they find application as protecting,[17] activating[18] and directing[19] groups as well. They can also act as catalysts in symmetry-forbidden reactions as is shown below for the formally (2π + 6π) cyclo-addition reaction of $(C_7H_8)Fe(CO)_3$ with diphenylacetylene, equation (2).[20]



(2)

Further examples of the coordination of unsaturated hydrocarbons to transition metals and the effect this exerts on the properties of the ligand will be encountered in the following sections.

2. Stereochemical Nonrigidity. Instrumentation, techniques, and mechanistic aspects.

Another interesting aspect of polyene transition metal complexes is the occurrence of stereochemically nonrigid molecules.[21] Molecules are designated stereochemically nonrigid if they undergo intramolecular rearrangements. The rates of these rearrangements usually influence NMR line shapes in the accessible temperature ranges. If all interconverting species are chemically and structurally equivalent then the molecules are called fluxional. Stereochemically nonrigid organometallic compounds have been reviewed by Cotton,[21,22] Vrieze,[23] Faller,[24] and Mann.[25]

The study of these nonrigid systems has been critically dependent on the available NMR instrumentation. In particular the recent developments in pulsed Fourier transform ^{13}C NMR spectroscopy have allowed the detection of carbonyl rearrangements[26a] and novel conformational interconversions.[26b] The greater chemical shift differences and the elimination of C-H coupling by broad-band ^{1}H decoupling make ^{13}C NMR spectroscopy eminently suited for the measurement of exchange rates.[27] The recent advances in hetero- and homonuclear double resonance techniques, i.e., proton noise decoupling, off-resonance decoupling, indor, and gated decoupling, have tremendously extended the range of ^{13}C NMR studies. Only the lower sensitivity of ^{13}C as compared to ^{1}H NMR spectroscopy can sometimes constitute a serious handicap.

Exchange rates (τ^{-1}), and therewith the activation parameters, can be determined by the line shape analysis of NMR spectra as a function of temperature,[22-25] by the spin-echo technique,[28] by the measurement of spin-lattice relaxation times (T_1-values),[29] by studying the pressure dependence of NMR spectra,[30] and by the Forsén-Hoffman spin saturation technique.[31] Experimental difficulties however often complicate the latter methods and variable temperature ^{1}H and ^{13}C NMR spectroscopy has been the most important technique for studying the mechanistic and energetic aspects of nonrigid organometallic molecules.

The determination of the energetics for the rearrangements is often accomplished by computer simulation of the NMR data. The usual input into the available programs is $\tau^{-1} = K$, where τ^{-1} is the reciprocal of the lifetime and K the overall rate constant for the process. A careful distinction between τ^{-1} and the rate of leaving each site must be made in order to avoid errors in the calculations of activation energies. For instance for a simple two-site exchange problem with equal populations the rate of leaving site 1, k_{12}, is equal to 0.5 K, i.e., $k_{12} + k_{21} = K$ or $k_{12} = k_{21} = 0.5$ K. Neglect of this relation produces errors of factors of 2 in the "rate" constant. Similar relations can be deduced for more complicated cases. Sources of error and related complications in using computer calculations of line shapes have been discussed by Allerhand *et al.*[32] and by Faller.[24]

We should also note at this junction that the rearrangement processes considered here, and in many other instances, are *intramolecular* in nature. Thus, the experimentally obtained entropies of activation, $\Delta S^{\ddagger}$, are rather small. An unusually large value of $\Delta S^{\ddagger}$ should therefore be regarded with suspicion. Most probably it is indicative of a poor experimental set of data and not of some fundamental property of the rearrangement mechanism. Further discussion on the factors affecting the errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be found in a very lucid discussion by Binsch.[33a]

To avoid the tedious computer simulation of the experimental spectra at all temperatures it is sometimes more practical to determine the rate constant as accurately as possible at one temperature and to obtain the corresponding value of $\Delta G^{\ddagger}$. In addition, for the simple two-site exchange problem with equal populations, approximate expressions to determine $\Delta G^{\ddagger}$ at the coalescence temperature are also known.[33] These are shown below.

$$k = \left(\frac{\pi}{\sqrt{2}}\right)\Delta\nu \qquad \text{two uncoupled sites} \qquad (3)$$

$$k = \left(\frac{\pi}{\sqrt{2}}\right)(\Delta\nu^2 + 6J^2)^{\frac{1}{2}} \qquad \text{coupled AB spin system} \qquad (4)$$

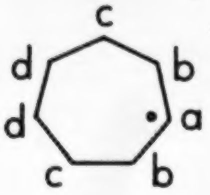
$$\Delta G^{\ddagger} = -RT_c \ln(h\pi\Delta\nu/\sqrt{2}\ kT_c) \qquad (5)$$

$$= 19.13\ T_c\ (9.97 + \log(T_c/\Delta\nu))\ \text{J mol}^{-1}. \qquad (6)$$

T_c = coalescence temperature; $\Delta\nu$ = chemical shift difference at T_c.

These expressions stem directly from the absolute rate theory and are sufficiently accurate for most purposes.[32,33] Often the chemical shift difference between the two sites is temperature dependent and $\Delta\nu$ has to be extrapolated from the slow exchange limit into the region of interest. Large errors in $\Delta G^{\ddagger}$ can result if this is not taken into account.[33a,b]

During the initial stages of the line broadening the linewidths of those resonances *from which nuclei leave faster will be broader* than the remaining resonances. This principle often makes it possible to elucidate the rearrangement mechanism. This is demonstrated in Scheme I. This scheme shows how the different environments are interchanged by three rearrangement pathways, the 1,2-, 1,3-, and the 1,4-shift mechanisms, for an η^n-C_7H_7 ring, n = 1,3 or 5, as applicable for example to $(\eta^3\text{-}C_7H_7)Co(CO)_3$[34] and



1,2-shift:

$$\begin{bmatrix} a \\ b \\ c \\ d \end{bmatrix} \longrightarrow \begin{bmatrix} b \\ a,c \\ b,d \\ c,d \end{bmatrix} \quad \text{d narrower}$$

1,3-shift:

$$\begin{bmatrix} a \\ b \\ c \\ d \end{bmatrix} \longrightarrow \begin{bmatrix} c \\ b,d \\ a,d \\ b,c \end{bmatrix} \quad \text{b narrower}$$

1,4-shift:

$$\begin{bmatrix} a \\ b \\ c \\ d \end{bmatrix} \longrightarrow \begin{bmatrix} d \\ c,d \\ c,b \\ a,b \end{bmatrix} \quad \text{c narrower}$$

Scheme I. The exchange of sites for different rearrangement pathways.

$(\eta^1\text{-}C_7H_7)SnPh_3$.[35] Only if an *unambiguous assignment* of all (or most) of the resonances is obtained can the dominant pathway be deduced. For example, a 1,2-shift is indicated by a slower collapse of the resonance d in Scheme I.

Cotton[22] and Faller[24] have reviewed the existing data on the migration of metals about cyclic conjugated unsaturated hydrocarbons and found that the majority of these rearrangements occur by the *1,2-shift* mechanism. However, apparent exceptions have been observed. Cotton and co-workers, for example, observed that the four ^{13}C resonances of the cyclooctatetraene ring in $(\eta^6\text{-}C_8H_8)Mo(CO)_3$ broadened equally on raising the temperature above that of the slow exchange limit.[36] This immediately eliminates the 1,2- and 1,4-shift as the dominant rearrangement pathway. A random pathway *via* a 20-electron, $\eta^8\text{-}C_8H_8$, "piano-stool" intermediate was proposed to explain these facts. This proposal has been criticized and a 16-electron, $\eta^4\text{-}C_8H_8$, species has been suggested as an intermediate.[37] This alternate pathway leads to either a dominant specific 1,3-shift or to a random shift. The latter 2 processes are indistinguishable by the experiments carried out by Cotton *et al*. The fluxional behaviour of the compound $(\eta^1\text{-}C_7H_7)Sn(C_6H_5)_3$ has been investigated and a 1,4- or 1,5-shift was deduced.*

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*The 1,4- and 1,5-shift mechanisms produce identical interconversions of the resonances of the seven-membered ring and are therefore indistinguishable for this compound.

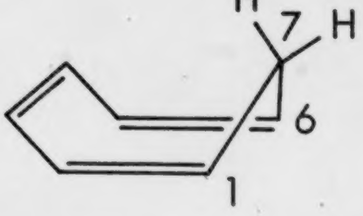
The Ph_3Sn group occupies the pseudo-axial position on the methylene carbon (endo conformation) and is thus situated in the more favourable position for the observed nonrigidity.[38] $(\eta^1\text{-}5\text{-}C_7H_9)SnPh_3$ also undergoes 1,5-shifts.[35b] These molecules and the related species $(\eta^1\text{-}5\text{-}C_7H_9)SnMe_3$[39] form the only organometallic compounds which undergo clearly established 1,5-shifts of the metallic moiety around the organic ligand.

The observation of 1,5-shifts is inconsistent with the principle of least motion, which was cited to account for the dominance of the 1,2-shift mechanism in transition metal complexes, but follows the prediction of the Woodward-Hoffman rules. The 1,2- and 1,5-pathways are degenerate (resulting in identical site exchanges) in the well-studied η^1-cyclopentadienyl derivatives of the transition metals but the $\eta^1\text{-}C_7H_7$ or $\eta^1\text{-}C_7H_9$ complexes would allow a distinction to be made between the two. However the preparation of such a transition metal complex has been accomplished only recently and mechanistic elucidation awaits further work.[51] Non-transition elements may satisfy the requirements for a concerted sigmatropic rearrangement and orbital symmetry rules may apply. The possible involvement of transtion metal d-orbitals however may result in a relaxation of the above rules and caution should be exercized in relating the experimental data and the derived operative mechanism to the factors controlling the mode of rearrangement in nonrigid transition metal organometallic species. As a matter of fact, interest has long centered on ways to alter the course of thermal or photochemical rearrangements by the presence of transition metals.[3]

Apparent 1,3-shift mechanisms are rather rare and have only been observed for (a) $(\eta^4\text{-}C_7H_8)Fe(CO)_3$[41] and its substituted derivatives, the study of which forms a major concern of this thesis, (b) $(\eta^6\text{-}C_8H_8)Cr(CO)_3$,[42] (c) $(\eta^3\text{-}C_7H_9)Pd(acac)$ and its neutral and cationic derivatives and related cyclooctadienyl complexes,[43] and (d) $Ru_2(CO)_5(C_{16}H_{16})$.[40] $(\eta^6\text{-}C_8H_8)Cr(CO)_3$ was shown to undergo a 1,3-shift by the Forsén-Hoffman spin saturation method.[31,42] As mentioned above, the variable temperature ^1H and ^{13}C NMR profiles did, initially, not allow for a distinction to be made between the 1,3- and random-shift pathways.[36] Selective irradiation of the resonances in the ^{13}C NMR spectra showed that the transfer of saturation is not random. Quantitative analysis of the spectra lead to a dominant 1,3-shift as suggested by Whitesides.[37] A competing but less pronounced 1,2-shift was also established while the new findings were confirmed by a reinvestigation of the V.T. ^{13}C NMR spectra.[42] The above spin saturation transfer or Forsén-Hoffman technique has been adequately described.[25.31] The method can be relevant for the correct assignment of resonances and allows for the measurement of slow exchange rates. As such the Forsén-Hoffman technique constitutes a useful complementary method for the determination of kinetic parameters (quantitative aspects of the Forsén-Hoffman technique will be described in detail in Chapter II).

3. The C_7H_8 and C_7H_7 ligand systems. A review of η^1- through η^7-bonding modes.

In contrast to the allyl and cyclopentadienyl ligand systems cycloheptatrienyl and cycloheptatriene have received relatively little attention as unsaturated coordinating moieties.[44] However, the cycloheptatrienyl group and its parent molecule 1,3,5-cycloheptatriene form a particularly interesting organic substrate system. The presence of three conjugated double bonds holds a promise for a wide variety of bonding modes (η^1 to η^7) upon coordination to different transition metal centers. Free cycloheptatriene adopts a boat conformation[45] and its formulation as a homobenzene has been discussed.[46]

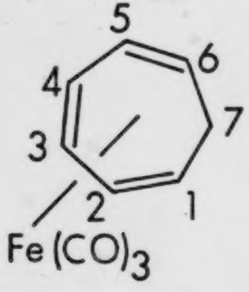


1

Photoelectron spectra[47] and NMR-studies[48] appear to indicate that overlap of the p_z-orbitals on C(1) and C(6) occurs and that these orbitals are slightly tilted towards each other. However, the low barrier to ring inversion (~25 kJ mol^{-1})[48,49] has been taken to indicate that the extent of this interaction is limited.

We now turn to a review of the different bonding modes of this ligand and its cycloheptatrienyl counterpart towards transition metal centers. Several of these bonding modes were encountered during the course of the present work and all are discussed in the following chapters as final reaction products or as rearrangement intermediates.

This review is by no means intended to be exhaustive and only the main characteristics of the different coordination patterns are described. Typical examples and leading references to the literature are given. A word of caution regarding the nomenclature is opportune. Throughout this thesis the hydrogen and carbon atoms of the cycloheptatriene and cycloheptatrienyl ligands are numbered as shown below for $(\eta^4\text{-}C_7H_8)Fe(CO)_3$ and $(\eta^3\text{-}C_7H_7)Co(CO)_3$, in accordance with the directions and



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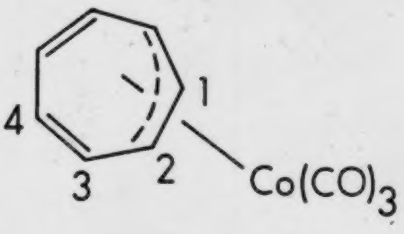

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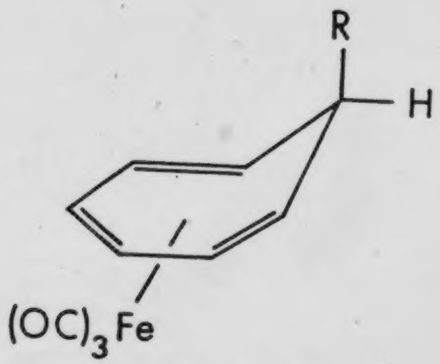
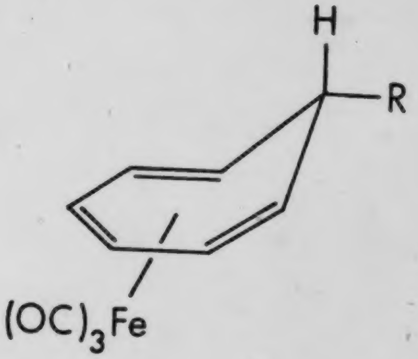
guidelines of the International Union of Pure and Applied Chemistry.[50] The η^1, η^2, η^5 and η^6 bonding modes are numbered similarly with the saturated carbon atom (η^2-, η^4-, and η^6-coordination) always carrying number seven and the central coordinated carbon atom in the η^1-, η^3-, and η^5-coordination modes carrying number one. The configurational designations *exo*- and *endo*- are defined with respect to the position of the ring-substituent relative to the transition metal moiety as exemplified for the (1-4-η-exo-7-RC_7H_7) and (1-4-η-endo-7-RC_7H_7)-tricarbonyliron complexes.



exo-R

$\underset{\sim}{4}$



endo-R

$\underset{\sim}{5}$

$\underline{\eta^1\text{-}C_7H_7}$

No monohapto cycloheptatrienyl derivatives of the transition metals have been reported.*

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*It now appears that (η^1-7-C_7H_7)Re(CO)$_5$ forms the first example of a monohapto cycloheptatrienyl complex of the transition metals.[51]

The reaction of organometallic anions with suitable precursors of the η^1-C_7H_7 ligand (C_7H_7Br, $C_7H_7C(O)Cl$, $C_7H_7OCH_3$, $C_7H_7{}^+BF_4{}^-$) constitutes one possible route towards the synthesis of representatives of this elusive class of compounds. This approach, however, suffers from two noticeable drawbacks. Decarbonylation often occurs upon the interaction of the precursor with metalcarbonyl anions resulting in the formation of η^3- or η^5-C_7H_7 compounds, equations [(7)-(9)].

$$[(C_5H_5)Fe(CO)_2]^- + C_7H_7{}^+BF_4{}^- \longrightarrow (\eta^3\text{-}C_7H_7)Fe(CO)(C_5H_5)\ ^{52,61} \quad (7)$$

$$[(OC)_4Co]^- + C_7H_7Br \longrightarrow (\eta^3\text{-}C_7H_7)Co(CO)_3\ ^{34,60} \quad (8)$$

$$[(OC)_5Mn]^- + C_7H_7C(O)Cl \xrightarrow[T\,=\,-70^\circ C]{} (\eta^5\text{-}C_7H_7)Mn(CO)_3\ ^{37} \quad (9)$$

In other instances an apparent electron-transfer reaction is frequently observed resulting in the formation of the thermodynamically very stable ditropyl (C_7H_7-C_7H_7) dimer and the dimeric metalcarbonyl, equations (10) and (11).

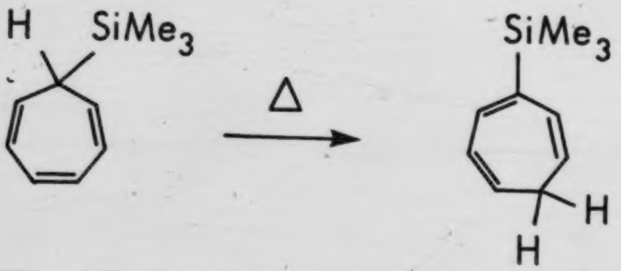
$$2[(OC)_5Mn]^- + 2C_7H_7C(O)Cl \xrightarrow{T\,=\,+20^\circ C} Mn_2(CO)_{10} + (C_7H_7)_2 + 2CO\ ^{37} \quad (10)$$

$$[(C_5H_5)Cr(CO)_3]^-Na^+ + C_7H_7Br \xrightarrow{-NaBr} [(C_5H_5)Cr(CO)_3]_2 + (C_7H_7)_2\ ^{53} \quad (11)$$

Formally the dimeric products arise from an electron transfer followed by the coupling of the radical fragments.

For the above manganese compound a rapid homolytic cleavage of the metal-carbon bond in a proposed $(\eta^1-C_7H_7)Mn(CO)_5$ intermediate has been suggested.[37] The high carbon-carbon bond strength in ditropyl (~160 kJ mol^{-1})[54] cetainly favors the irreversible formation of the dimeric products. Similarly Deganello and co-workers[55] have reported the formation of $((C_7H_7)Fe(CO)_3)_2$ from the reaction of $[(C_7H_7)Fe(CO)_3]^-$ with allyl halides.[55]

One set of monohapto cycloheptatrienyl derivatives of the main group elements deserve to be mentioned here: the compounds $(\eta^1-7-C_7H_7)MR_3$, M = Si, Ge, Sn with R = Ph[35] and M = Si, R = Me.[57] The interesting fluxional behaviour of the tin derivative has been commented upon already. On the other hand, Ashe[57] found that the 1,5-hydrogen shift is faster than the 1,5-trimethylsilyl shift in the silicon derivative, Scheme II.



Scheme II. The 1,5-hydrogen shift in $(\eta^1-7-C_7H_7)Si(CH_3)_3$.

$\eta^2-C_7H_8$

Few $\eta^2-C_7H_8$ complexes are known. Pauson and coworkers identified an η^2-intermediate in the synthesis of $(\eta^6-C_7H_8)Mn(C_5H_5)$ by infrared spectroscopy, equation (12).[58]

$$(C_5H_5Mn(CO)_3 \xrightarrow[h\nu,\,-CO]{C_7H_8} (\eta^2\text{-}C_7H_8)Mn(CO)_2(C_5H_5)$$

$$\nu_{CO}\text{: } 1965(vs),\ 1908(vs)$$

$$h\nu \Big\downarrow -2CO \qquad (12)$$

$$(\eta^6\text{-}C_7H_8)Mn(C_5H_5)$$

When 7-substituted cycloheptatrienes were employed (R = Ph, Me, t-Bu) mixtures of *exo* and *endo* η^6-isomers resulted. This aspect of the chemistry will be detailed below. The above η^2-complex, $(\eta^2\text{-}C_7H_8)Mn(CO)_2(C_5H_5)$, has recently been isolated as a yellow crystalline solid.[59] The ^{13}C NMR spectrum indicates that the cycloheptatriene ligand is coordinated through a double bond adjacent to the ring methylene carbon.

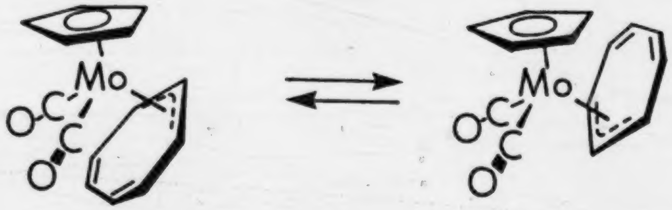
$\eta^3\text{-}C_7H_7$

Several $\eta^3\text{-}C_7H_7$ complexes of the transition metals have been synthesized. A summary of the relevant compounds, with respect to the complexes described in the following chapters, is given in Table I. In all cases the cycloheptatrienyl ligand is bonded to the metal center *via* an allyl moiety. This is most clearly demonstrated by the solid state structure of $(\eta^3\text{-}C_7H_7)Mo(CO)_2(\eta\text{-}C_5H_5)$, Figure III. Four carbonyl stretching frequencies are observed in the infrared spectra (in cyclohexane) of the latter compound indicating the presence of two conformers, $\underset{\sim}{8a}$ and $\underset{\sim}{8b}$.

TABLE I

(η^3-C_7H_7) complexes of the transition metals.

Compound	Reference
(η^3-C_7H_7)Mo(CO)$_2$(C_5H_5), 8	60, 63, 64
(η^3-C_7H_7)Co(CO)$_3$, 3	34, 60
(η^3-C_7H_7)Fe(CO)(C_5H_5), 9	52, 61
(η^3-C_7H_7)Mo(CO)$_2$L, 10 L = HBpz$_3$, H_2B(dimethylpyrazolyl)$_2$ PhBpz$_3$, HB(dimethylpyrazolyl)$_3$ Bpz$_4$	62
trans-μ-(1-4-η:5-7-η-C_7H_7)Fe(CO)$_3$Mo(CO_2)L, 11 L = C_5H_5, HBpz$_3$	62c, 64



8a 8b

Moreover a sharp resonance is evident for the cycloheptatrienyl protons in the ^1H NMR spectra of all the compounds listed in Table I at or above ambient temperature establishing the fluxional nature of the C_7H_7 moiety in these complexes.

The uncoordinated diene part of the seven-membered ring is available for coordination to a second transition metal, for example to the $Fe(CO)_3$ moiety. A structurally characterized, representative example of this new class of compounds is depicted in Figure IV.[64]

η^4-C_7H_8

The $Fe(CO)_3$ moiety demonstrates a pronounced tendency to coordinate preferentially to conjugated dienes.[1,65,66,67] The formation of $(\eta^4\text{-}C_7H_8)Fe(CO)_3$ in the thermal reaction of C_7H_8 with $Fe(CO)_5$ is therefore not surprising.*[68] The rather more elusive ruthenium analogue $(\eta^4\text{-}C_7H_8)Ru(CO)_3$

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[*] Although the large number of (conjugated diene)iron tricarbonyl complexes characterized to date supports this empirical observation, it was not so well-defined in the early days of organometallic chemistry. Indeed $(\eta^4\text{-}C_7H_8)\text{-}Fe(CO)_3$ was initially formulated as a dicarbonyl complex, $(\eta^6\text{-}C_7H_8)Fe(CO)_2$.[69]

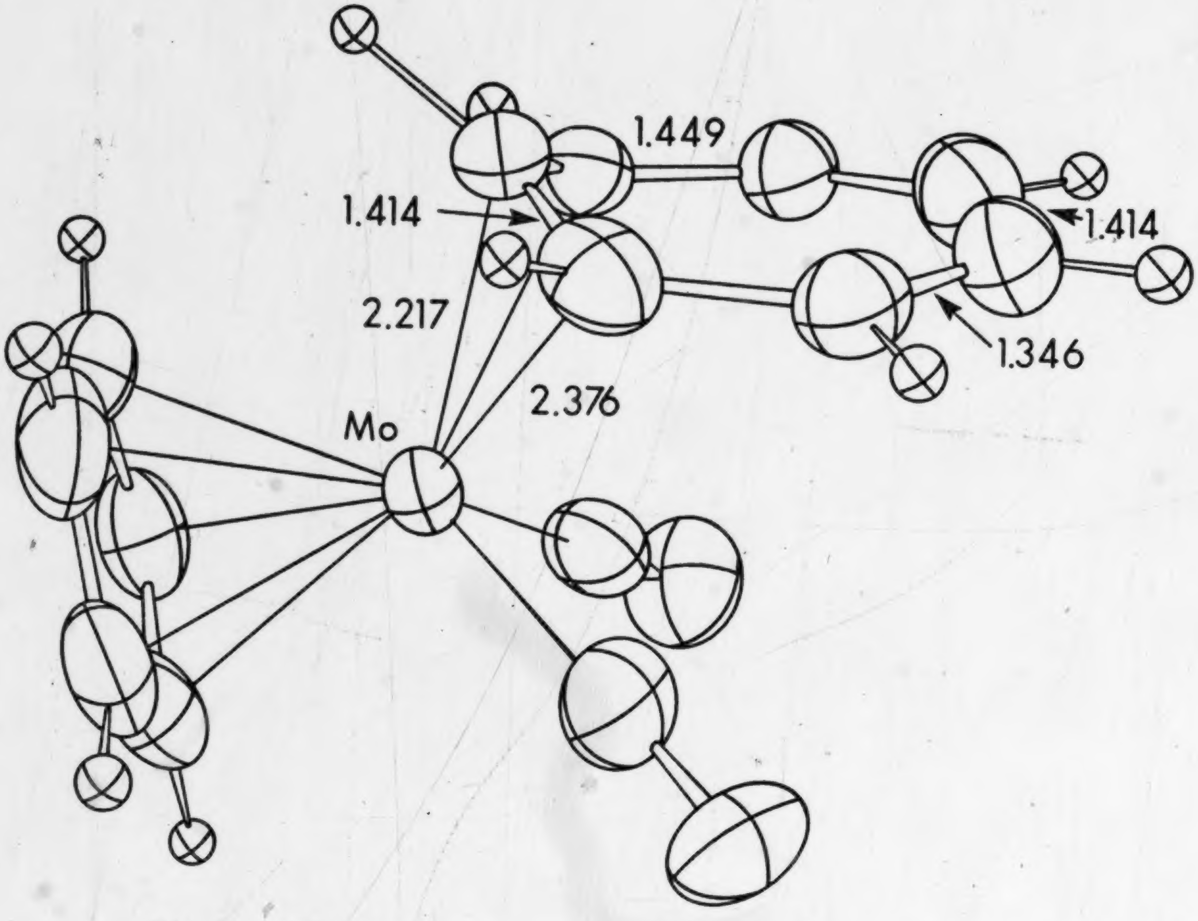
1.449
1.414
1.414
2.217
1.346
2.376
Mo

Figure III. Molecular structure of $(\eta^3\text{-}C_7H_7)Mo(CO)_2(C_5H_5)$.[64]

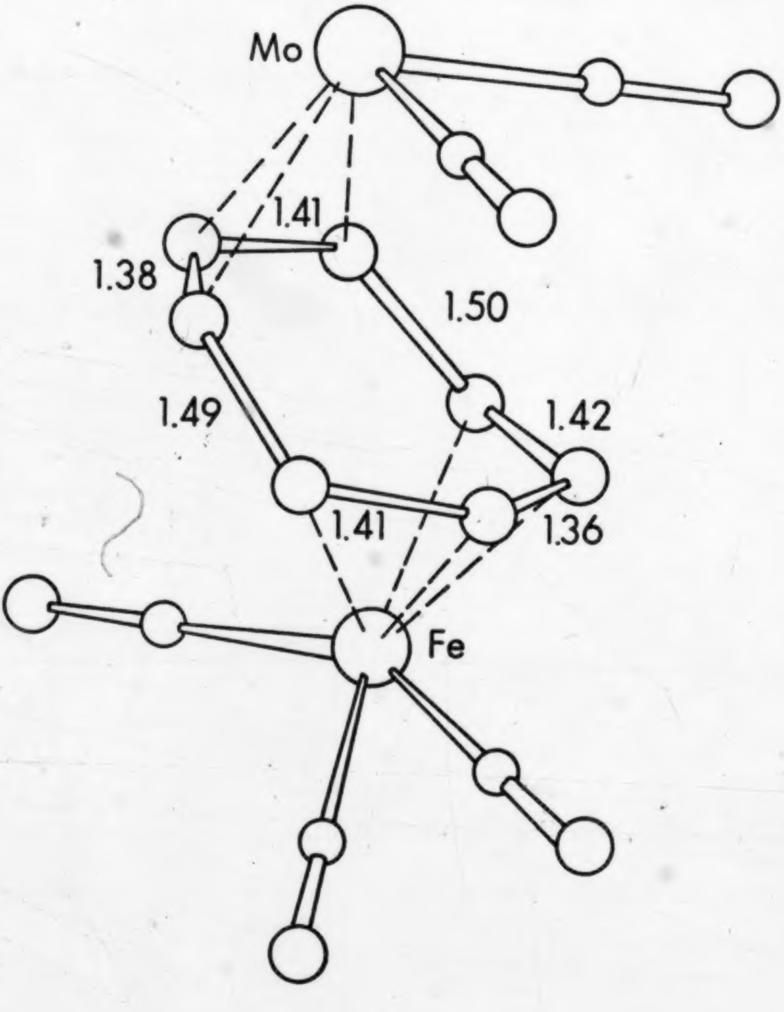
Mo
1.41
1.38
1.50
1.49
1.42
1.41
1.36
Fe

Figure IV. Molecular structure of trans-μ-(1-4-η:5-7-η-C_7H_7)Fe(CO)$_3$Mo(CO)$_2$(C_5H_5).[64] The C_5H_5 ligand is omitted for clarity.

was first prepared by Lewis[70] and has recently been synthesized from the reaction of Ru(η^4-C_8H_{12})(η^6-C_8H_{10}) with C_7H_8 under an atmosphere of carbon monoxide.[71] Mono- and polynuclear η^4- and η^6- cycloheptatriene complexes of iron, ruthenium and osmium have been reviewed by Deganello and coworkers.[67]

Substituted (η^4-C_7H_7R)Fe(CO)$_3$ complexes have also been prepared by the reaction of the appropriate organic moiety, C_7H_7R, with Fe(CO)$_5$ or Fe$_2$(CO)$_9$,[41c,72,73] by the addition of nucleophiles to [(C_7H_7)Fe(CO)$_3$]$^+$,[73] and by the electrophilic attack on [(C_7H_7)Fe(CO)$_3$]$^-$.[41a,b,55,74] The crystal structure of (exo-7-phenylcycloheptatriene)tricarbonyliron exhibits the characteristics of an η^4-coordinated cycloheptatriene ligand.[75] A schematic representation of this molecule is shown in Figure V. It is noted that (exo-7-PhC_7H_7)Fe(CO)$_3$ is the first structurally characterized simple cycloheptatrienetricarbonyliron complex. The structural features of related diazulene, tropone and azepine derivatives of tricarbonyliron have been compared.[75]

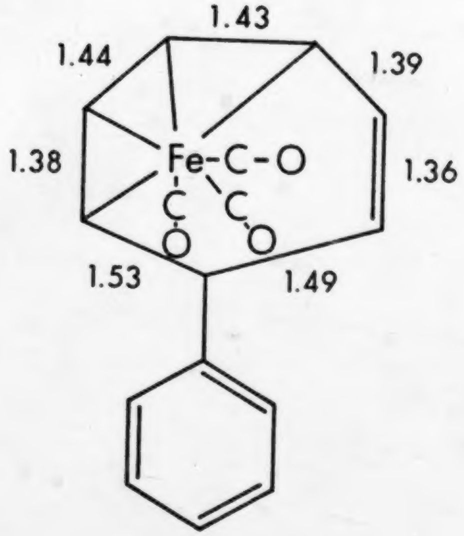

Figure V. Schematic representation of (exo-7-PhC_7H_7)-Fe$(CO)_3$.[75]

The phenyl substituent in the above complex is found to be positioned *exo* with respect to the Fe$(CO)_3$ group. The deviation from the long-short-long pattern expected for the bond lengths of the coordinated diene moiety has been attributed to the presence of a third uncoordinated double bond in this molecule.[75] Interestingly, the corresponding reaction with Cr$(CO)_6$ yielded a mixture of *endo and exo* isomers,[88] the bonding requirements of the metal carbonyl moiety appearently having an effect on the stereochemical outcome of the reaction.

Although η^4-coordination of poly-unsaturated organic ligands is most frequently observed with Fe$(CO)_3$*, other metal carbonyl moieties also show this bonding mode. The coordination of two non-conjugated double bonds in C_7H_8 to a transition metal fragment has been observed in $(\eta^4-C_7H_8)Rh(acac)$, 12.[76] Significantly the coordination here is through the non-conjugated 1,5-double bonds and

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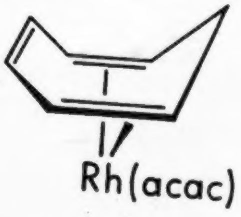
*For the complexation of a non-conjugated diene to Fe$(CO)_3$ see reference 65b.



12

not through the 1,3-diene fragment as it is observed with $Fe(CO)_3$. One further mode of coordination in which four carbon atoms of the cycloheptatriene ring are in a bonding interaction with the metal atom is to be mentioned. The 1,3 (or 1,5) addition of electrophiles to $(C_7H_8)Fe(CO)_3$ results in the formation of a new type of species.[78,79,80] In these compounds the iron atom achieves an 18 electron configuration by the coordination of the organic moiety *via* an η^3-allyl group and a σ-bonded carbon atom in addition to the coordination of the three carbonyl ligands.[78] The product from the reaction of $(C_7H_8)Fe(CO)_3$ with tetracyanoethene has been characterized by X-ray crystallography and is shown in Figure VI.

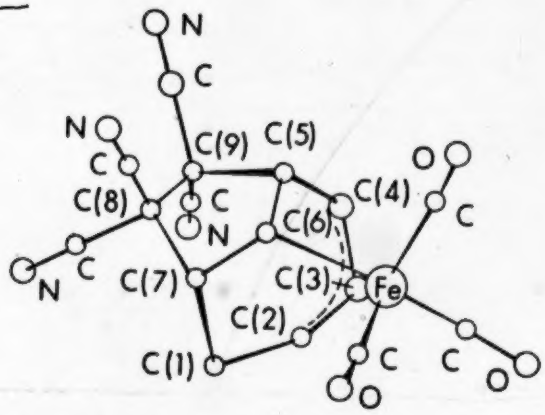


Figure VI. Structure of the cycloheptatrienetricarbonyl-iron-tetracyanoethene adduct.[78]

η^5-C_7H_7

Only three neutral organometallic complexes containing the η^5-C_7H_7 moiety have been described.[37,81,82] Whitesides and Budnik have reported the synthesis of $(\eta^5\text{-}C_7H_7)Mn(CO)_3$ from the low-temperature decarbonylation of $(C_7H_7C(O))Mn(CO)_5$.[37] The 1,2-shift was established, by variable temperature ^{13}C NMR spectroscopy, as the mechanism responsible for the interchanging of the carbon atom positions of the ring.

The interesting species (1-5-η-cycloheptatrienyl)-(1-5-η-cycloheptadienyl)iron, 13,[81] and its ruthenium[82] analog, 14, have been synthesized. In addition to the high temperature 1,2-shift apparent for the η^5-C_7H_7 ring a second exchange process was observed at lower temperatures for the iron compound. This latter process, identified as a rocking motion of the rings

($\Delta G^{\ddagger}$ = 40 ± 6 kJ mol^{-1} *versus* 71 ± 10 kJ mol^{-1} for the 1,2-shift) imposes an apparent plane of symmetry upon each of the two seven-membered rings.[81] In agreement with the X-ray structure, Figure VII, the low temperature limiting

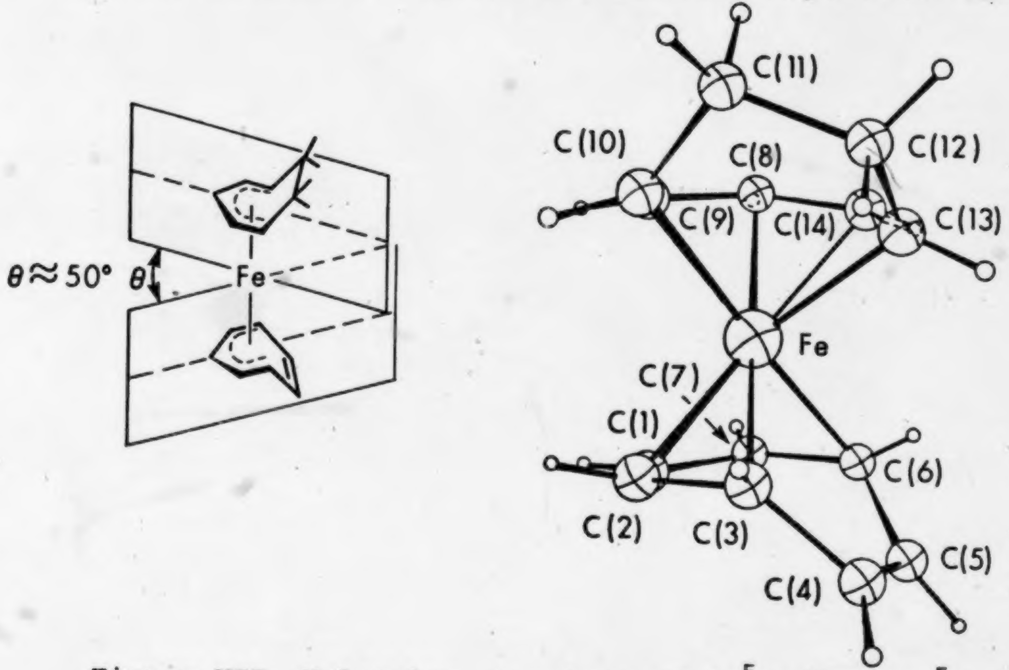


Figure VII. Molecular structure of $(\eta^5\text{-}C_7H_7)Fe(\eta^5\text{-}C_7H_9)$.[81] A schematic representation of one of the two interconverting forms of 13 is shown on the left.

^{13}C NMR spectrum showed 14 inequivalent carbon signals. In addition to the above neutral $\eta^5\text{-}C_7H_7$ compounds only one other mononuclear $\eta^5\text{-}C_7H_7$ metal complex has been reported,* namely $[(C_7H_7)Fe(CO)_3]^+$, 15, by Pettit and coworkers in 1964.[73]

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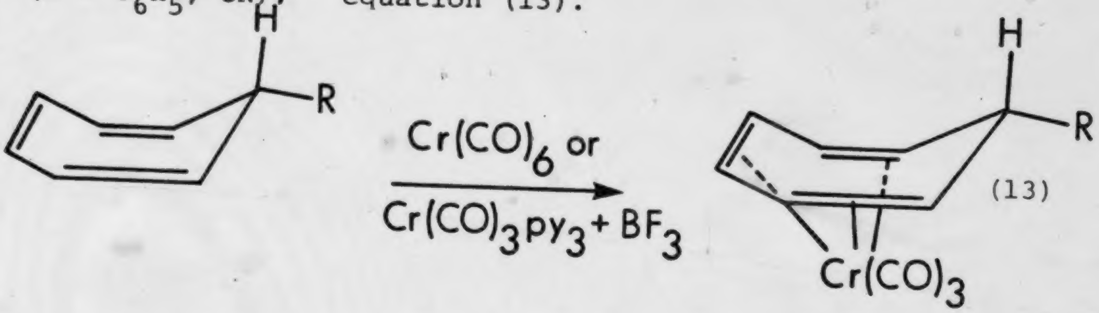
* $(\eta^5\text{-}C_7H_7)M(CO)_3I$, M = Mo, W, has been proposed as an intermediate in the reaction of $[(C_7H_7)M(CO)_3]^+$ with I^-. The final product of this reaction is $(\eta^7\text{-}C_7H_7)M(CO)_2I$.[84]

An elegant theoretical study by Whitesides,[85] using photoelectron spectroscopy and molecular orbital calculations, accounted for the observed differences in the activation parameters for the 1,2-shift mechanism in $[(\eta^5\text{-}C_7H_7)Fe(CO)_3]^+$ and $(\eta^5\text{-}C_7H_7)Mn(CO)_3$ ($T_c \cong -50°C$, $E_a \cong 46$ kJ mol^{-1}, and $T_c \cong +20°C$, $E_a \cong 63$ kJ mol^{-1}, respectively). These differences were correlated with the extent of back-bonding to the ring. An increase in back-bonding to the seven-membered ring resulting in an increase in the barrier to migration. An increase in positive charge on the metal thus leads to a faster rate of rearrangement.[83,85]

$\underline{\eta^6\text{-}C_7H_8}$

Several transition metal derivatives of the type $[(\eta^6\text{-}C_7H_8)ML_n]^{m+}$, L = CO, PR_3, diene, arene, m = 0, 1, and n = 1-3, have been reported. Two of the earliest representatives of this class of compounds are $(\eta^6\text{-}C_7H_8)$-$Cr(CO)_3$ and $(\eta^6\text{-}C_7H_8)Mo(CO)_3$ prepared by the direct thermal reaction of cycloheptatriene with the parent carbonyl.[77] The crystal and molecular structure of the latter compound has been reported.[86] Several $(\eta^6\text{-}C_7H_8)Mo(CO)_2L$, L = phosphine, complexes have been synthesized by the borohydride reduction of the corresponding $[(\eta^7\text{-}C_7H_7)Mo(CO)_2L]^+$ cations.[87]

Substituted cycloheptatriene derivatives of the metal moieties Mn(C_5H_5) and $Cr(CO)_3$ have been studied by Pauson and coworkers.[88] Nucleophilic attack on $[(C_7H_7)Cr(CO)_3]^+$ has invariably resulted in the formation of the *exo* isomer, $(\eta^6$-exo-$C_7H_7R)Cr(CO)_3$. This is in contrast to the direct thermal reaction of substituted 1,3,5-cycloheptatrienes with $Cr(CO)_6$ which produced either exclusively the *endo* isomers (R = CH_3, $CH_2CO_2C_2H_5$, $CH(CO_2C_2H_5)_2$, $CH_2C \equiv CH$) or a mixture of the *endo* and *exo* isomers (R = C_6H_5, CN),[88] equation (13).



(13)

R = $CH_2CO_2C_2H_5$

Since the free substituted cycloheptatrienes exist preferentially in the equatorial boat conformation[45,89] the formation of the *endo* isomer can be understood if the reaction occurs without ring inversion. In the two cases where both *exo* and *endo* isomers are observed the presence of a relatively large amount of axial isomer or a metal induced ring inversion is suggested.[88] The relevant bond lengths and angles for the seven-membered ring in (exo-7-phenylcycloheptatriene)chromium tricarbonyl are schematically reproduced in Figure VIII.[90] The complexed

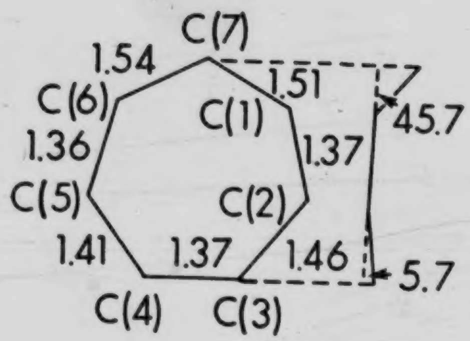


Figure VIII. Schematic representation of the seven-membered ring in (exo-7-C_7H_7Ph)Cr$(CO)_3$.[90]

cycloheptatriene ligand retains the alternation of bond lengths shown in the free molecule[89] but the conjugated system is considerably flattened upon coordination.[89,90]

Of these isomeric complexes only the *exo* isomer, containing a pseudo-equatorial hydrogen rearranges when heated.[99] This reaction has been classified as a metal-assisted 1,5 sigmatropic* shift although the mechanism of this assiatance is still rather obscure. Previously Roth and Grimme[101] found a similar conformational preference for the migration of hydrogen in the unsubstituted complex, Scheme III. Uncomplexed cycloheptatriene undergoes migration of the pseudo-axial hydrogen only.[102]

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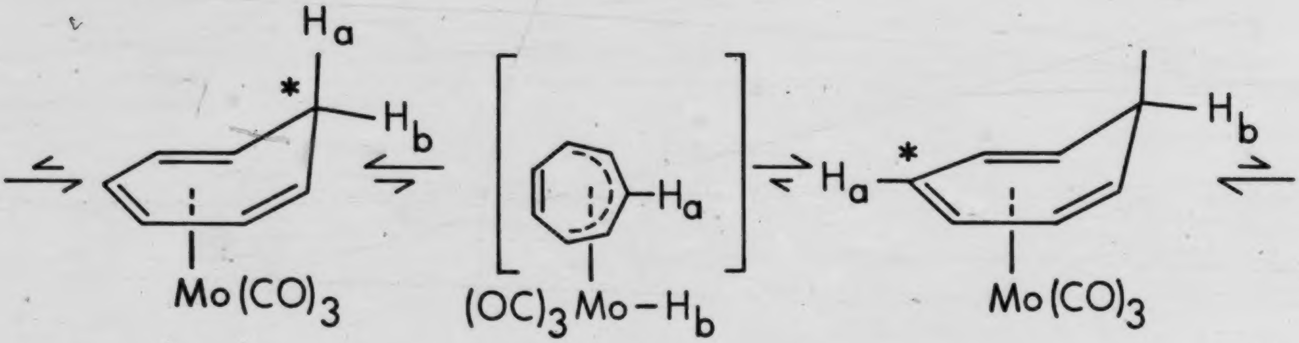
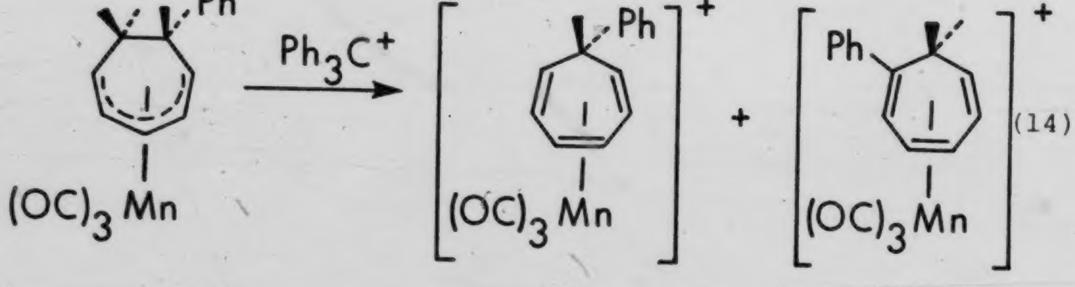
* For a review of sigmatropic rearrangements see reference 100.



Scheme III. Stereochemistry of the hydrogen migration in $(C_7H_8)Mo(CO)_3$.[101]

Similar results were observed in the photochemical reaction of substituted cycloheptatrienes C_7H_7R with $(C_5H_5)Mn(CO)_3$.[58] For R = Ph, Me, and t-Bu mixtures of the *exo* and *endo* isomers were obtained. The displacement of all three carbonyl ligands in $(C_5H_5)Mn(CO)_3$ by C_7H_8 *via* the intermediate $(\eta^2\text{-}C_7H_8)Mn(CO)_2(C_5H_5)$ was mentioned before under the $\eta^2\text{-}C_7H_8$ compounds.[58] The crystal structure of $(CH_3C_5H_4)Mn(\eta^6\text{-exo-7-PhC}_7H_7)$ has been described.[92] Hydride abstraction from $(\eta^5\text{-endo-6-}C_7H_8Ph)Mn(CO)_3$ results in a mixture of 2 isomers of $[(\eta^6\text{-}C_7H_7Ph)Mn(CO)_3]^+BF_4^-$,[93] equation (14).



(14)

Exo hydride abstraction by Ph_3C^+ occurs and the *endo* isomer is obtained as the major component.

An η^6-C_7H_8 derivative of iron tricarbonyl has also been reported[94] $(\eta^6\text{-}C_7H_8)Ru(\eta^4\text{-}C_8H_{12})$ can be synthesized from $Ru(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_8H_{10})$ and cycloheptatriene under a hydrogen atmosphere,[71a] while $(\eta^6\text{-}C_7H_8)Ru(CO)_2$ was isolated as a byproduct in the reaction of the same starting material with CO and C_7H_8. $(\eta^6\text{-}C_7H_8)Ru(\eta^4\text{-}C_8H_{12})$ can also be obtained *via* the Grignard mathod by reacting $[(C_8H_{12})\text{-}RuCl_2]_2$ with $i\text{-}C_3H_7MgBr$ in the presence of C_7H_8.[95]

$\underline{\eta^7\text{-}C_7H_7}$

Many η^7-C_7H_7 (or η-C_7H_7) derivatives of the transition metals are known.[96,97] To demonstrate the planarity of the seven-membered ring in these complexes the molecular structure of $[(C_7H_7)Mo(CO)_3]^+BF_4^-$ is shown in Figure IX.[97]

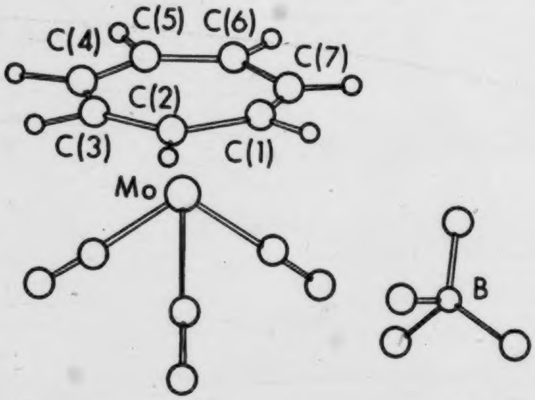


Figure IX. Molecular Structure of $[(C_7H_7)Mo(CO)_3]^+BF_4^-$.[97]

The average value of the C-C distances in this cation is 1.40 Å and the average value of the internal C-C-C angles is 128.4°, the theoretical value for D_{7h}-symmetry being 128.6°. The C_7-ring appears as a fully delocalized planar system with the central metal being equidistant from all seven ring carbon atoms.[97]. The decrease in the reactivity of $C_7H_7^+$ towards nucleophiles upon coordination to the $Cr(CO)_3$ moiety has been discussed by Clark *et al.*[98]

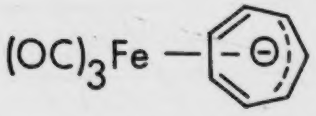
4. Molecular orbital description, structure, and stereochemical nonrigidity of the anion $[(C_7H_7)Fe(CO)_3]^-$.

The unique characteristics imparted to the antiaromatic molecules C_4H_4 and C_8H_8 by their coordination to transition metal moieties are also observed with the anion $C_7H_7^-$. The modification of the ligand properties upon coordination is particularly well demonstrated by the difference in acidity between free and complexed cycloheptatriene, equation (15).

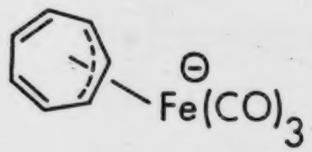
$$C_7H_8 \rightleftharpoons C_7H_7^- + H^+ \tag{15}$$

1,3,5-cycloheptatriene is an extremely weak acid. The pK_a for the above equilibrium has been estimated to be greater than 38.[103] The free anion $C_7H_7^-$ is not well characterized[103] and no satisfactory syntheses have been reported.[103,104] In contrast (η^4-cycloheptatriene)tricarbonyliron, $\underset{\sim}{2}$, is quantitatively deprotonated to give $[(C_7H_7)Fe(CO)_3]^-$.[105] Moreover, as first shown by Maltz and Kelly,[105] specific exo-7-deuteration can be easily accomplished for $\underset{\sim}{2}$ by treatment with $NaOCH_3$ in CH_3OD for 1 h at ambient temperature. A similar reaction, carried out at elevated temperatures for 24 h, with cycloheptatriene did not result in detectible deuterium incorporation.[104] The suggested *exo*-deuteration has been confirmed recently by Brookhart.[106] It will be shown in Chapter II that the pK_a of $(C_7H_8)Fe(CO)_3$ is considerably lower than that of free cycloheptatriene.

In accordance with the 18 electron rule two structural alternatives can be proposed for the structure of the $[(C_7H_7)Fe(CO)_3]^-$ anion.



16a



16b

Structure **16a** is characterized by an η^4-coordinated butadiene moiety which is part of the seven-membered ring. The uncoordinated allyl anion fragment formally carries the negative charge. In **16b** the ring is bonded to the iron center through the allyl group leaving an uncomplexed butadiene unit within the ring while the negative charge is formally localized on the (allyl)$Fe(CO)_3$ moiety. The assumption that the anion exists in solution as an equilibrium mixture of these two isomeric forms has also been made.[55] The room temperature ^1H NMR spectrum of the anion shows a single sharp line indicative of a fluxional molecule and/or of a facile interconversion between **16a**

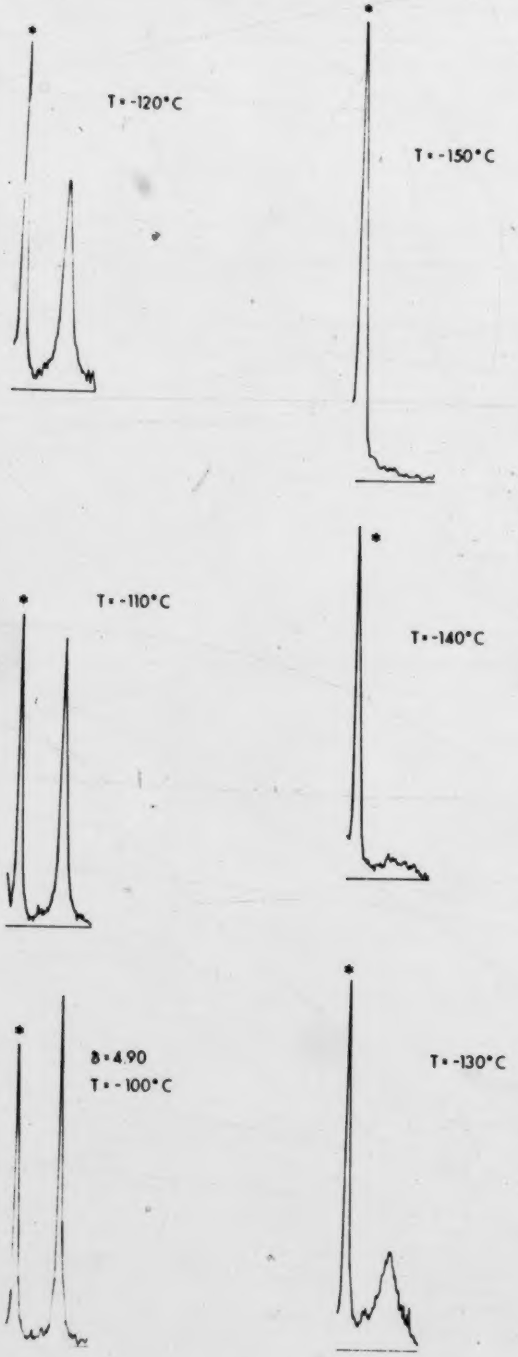


Figure X. Variable Temperature ^{1}H NMR Spectra of $[PPN]^+[C_7H_7Fe(CO)_3]^-$ in CHF_2Cl/CD_2Cl_2 (4/1). (*Indicates residual $CHDCl_2$ at $\delta = 5.32$).

and **16b**.

In view of these facts molecular orbital calculations initiated in order to obtain further insight into the structural preference and the rearrangement barrier for anion **16** were well warranted.[83] During the course of the work described in this thesis the crystal structure of **16** (as the $(C_6H_5)_4As^+$ salt) was reported.[107] Because both the extended Hückel calculations and the crystallographic structure determination are highly relevant to the solid state and solution structures of **16**, to the chemical reactivity and to the activation parameters for the fluxional processes of the compounds described here, the salient features of the above studies are discussed below.

The molecular orbital calculations on $[(C_7H_7)Fe(CO)_3]^-$ were performed using a geometrically simplified model for **16**.[83] The cycloheptatrienyl ligand was considered to be planar with D_{7h} local symmetry, and the $Fe(CO)_3$ fragment was constrained to a local C_{3v} symmetry with all C-Fe-C angles being 90°. The important molecular orbitals of the $Fe(CO)_3$ fragment and of the $C_7H_7^-$ ion are shown in Figure XI. A detailed derivation of the molecular orbitals has been given[108] and discussed.[2b,83,108,109] Figure XII shows the calculated energy profiles which result upon

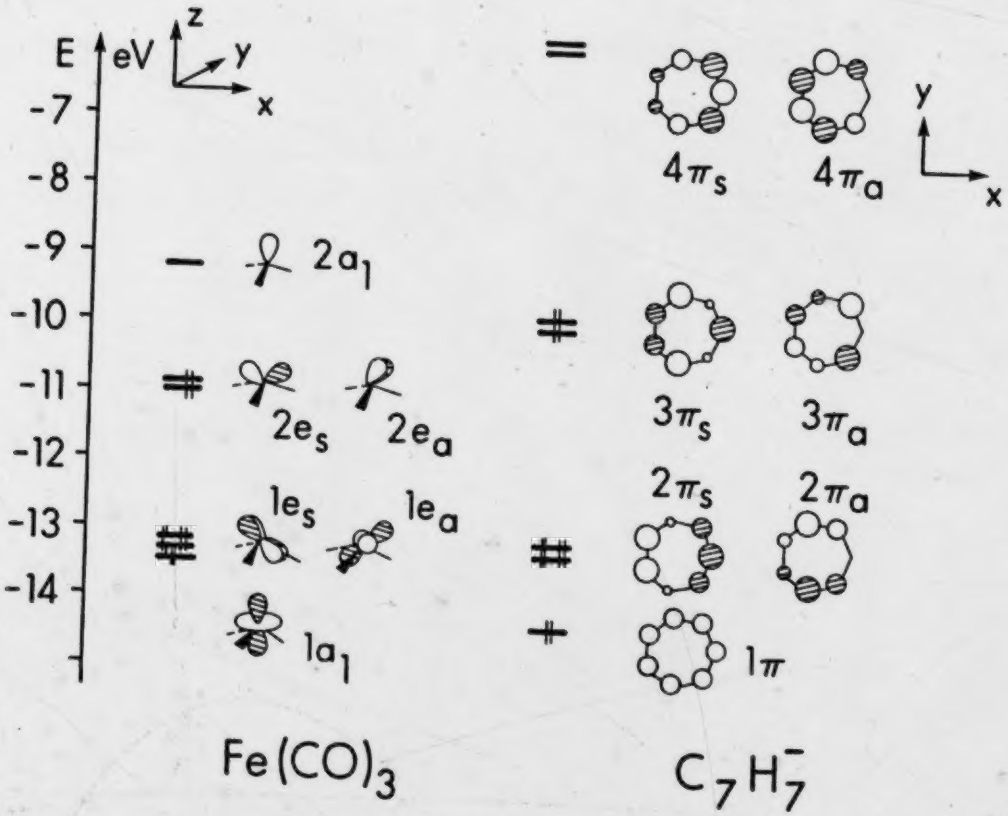

E
eV
z
y
x
-7
-8
-9
-10
-11
-12
-13
-14
2a1
2es
2ea
1es
1ea
1a1
4πs
4πa
3πs
3πa
2πs
2πa
1π
y
x
Fe(CO)3
C7H7−

Figure XI. Molecular orbitals of the $Fe(CO)_3$ and $C_7H_7^-$ moieties.[83]

changing the coordination of the cycloheptatrienyl ligand from η^2 *via* η^4 to η^7 and from η^1 *via* η^3 to η^7. The iron center is positioned in the mirror plane of the ligand at 1.8 Å below the plane of the cycloheptatrienyl group during these changes. In each case a well-defined energy minimum is observed for the η^4-diene or η^3-allyl coordination

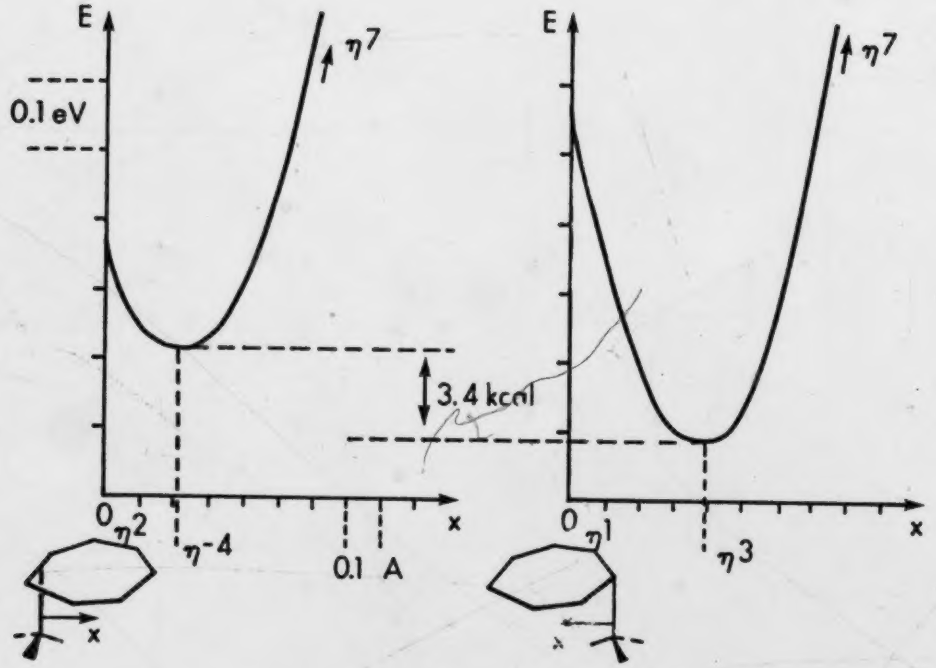


Figure XII. Calculated energy profiles for the $[(C_7H_7)\text{-}Fe(CO)_3]^-$ anion as a function of the coordination number.[83]

mode. Moreover the η^3-coordination mode is found to be favoured by about 14.2 kJ mol^{-1}. The vital differences between the two minima are represented in the partial molecular orbital diagram depicted in Figure XIII.* The main contribution to the formation of these two minima arises from the bonding interactions which

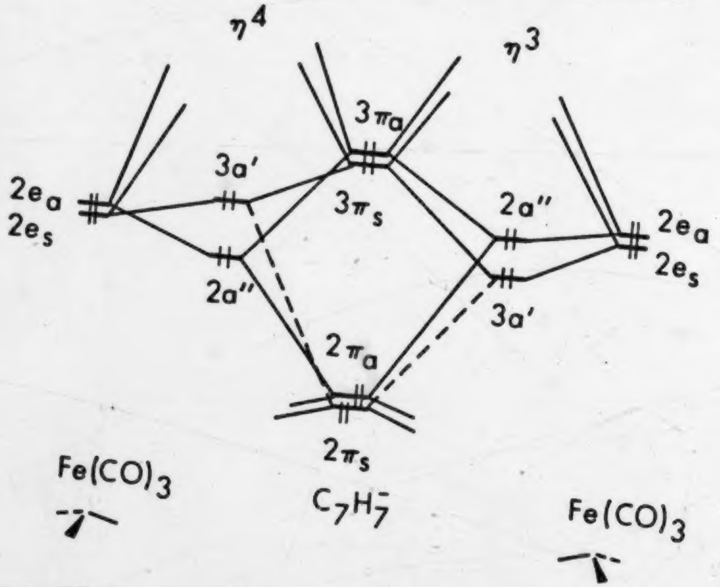


Figure XIII. Partial molecular orbital diagram of $[(C_7H_7)Fe(CO)_3]^-$.[83]

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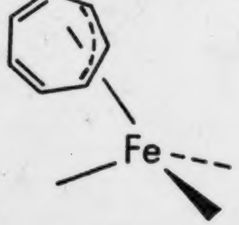
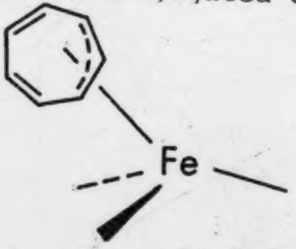
[*] Throughout this discussion a staggered geometry as in 16c below is assumed. The eclipsed conformer 16d is energetically less favoured for related conjugated diene and



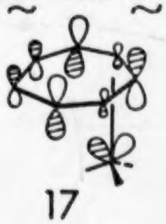
16c



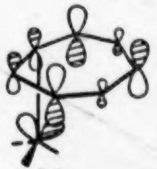
16d

cyclopentadienyl complexes.[2b,109b] It is noted that both the conformational preference of 16c over 16d and the difference in energy content between the two isomeric structures 16a and 16b arise to a large extent from the asymmetry of the Fe(CO)$_3$ fragment orbitals. This in turn is due to the mixing of the 1e (mainly d_{xy} and $d_{x^2-y^2}$ in character) and 2e (mainly d_{xz} and d_{yz}) levels of the Fe(CO)$_3$ unit.[2b]

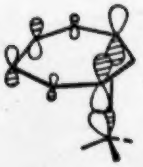
occur between the 2e and 3π orbitals upon changing the coordination from η^1 (or η^2) to η^7. These interactions are shown below for the $3\pi_s$ and $2e_s$ (**17** and **18**) and the $3\pi_a$ and $2e_a$ (**19** and **20**) pairs.



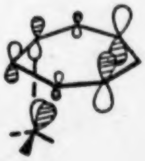
17



18



19



20

The above interactions diminish rapidly if the $Fe(CO)_3$ fragment is moved towards the center of the ring (η^7-coordination) indicating that a symmetrical intermediate in which the iron atom is equidistant from all ring carbon atoms is unlikely as a rearrangement intermediate. Depopulation of the 3a' and 2a", as in $[(C_7H_7)Cr(CO)_3]^+$, however favours the η^7-geometry.[37,83]

It is interesting to observe that the molecular orbital calculations indicate a *higher* negative charge on the C_7H_7 ligand for structure **16b** as compared to **16a**. The substantial localization of the 2a" orbital on the uncoordinated diene part of the ring, in **16b**, is responsible for this and predicts an alternation of the C-C bond lengths in the diene fragment. One final comment with respect to the in 17 through 20 indicated interactions must be made. These representations show the presence of antibonding interactions between the $Fe(CO)_3$ fragment and the uncoordinated part of the ring. This points towards a non-planar structure for the cycloheptatrienyl ligand. Indeed, if the initial requirement of a planar C_7H_7 ring is relaxed while maintaining planar butadiene and allyl units and fixing the position of the $Fe(CO)_3$ group at the above obtained minima, a tilt angle of ~40° is derived from additional calculations.[83]

To summarize the results of the extended - Hückel calculations on $[(C_7H_7)Fe(CO)_3]^-$ one can note that:
(i) the ground state structural preference is for an η^3-coordinated cycloheptatrienyl group, structure 16b, and (ii) the free energy of activation for the rearrangement process which exchanges all carbon atoms is very small. This process, which likely proceeds through the intermediacy of 16a, is probably best described as a 1,2 shift of the $Fe(CO)_3$ fragment.

The determination of the crystal and molecular structure of $[(C_7H_7)Fe(CO)_3]^-AsPh_4^+$ by Behrens and coworkers[107] allowed a comparison to be made between the theoretical predictions and the experimental facts. The structure of the anion is depicted in Figure XIV while

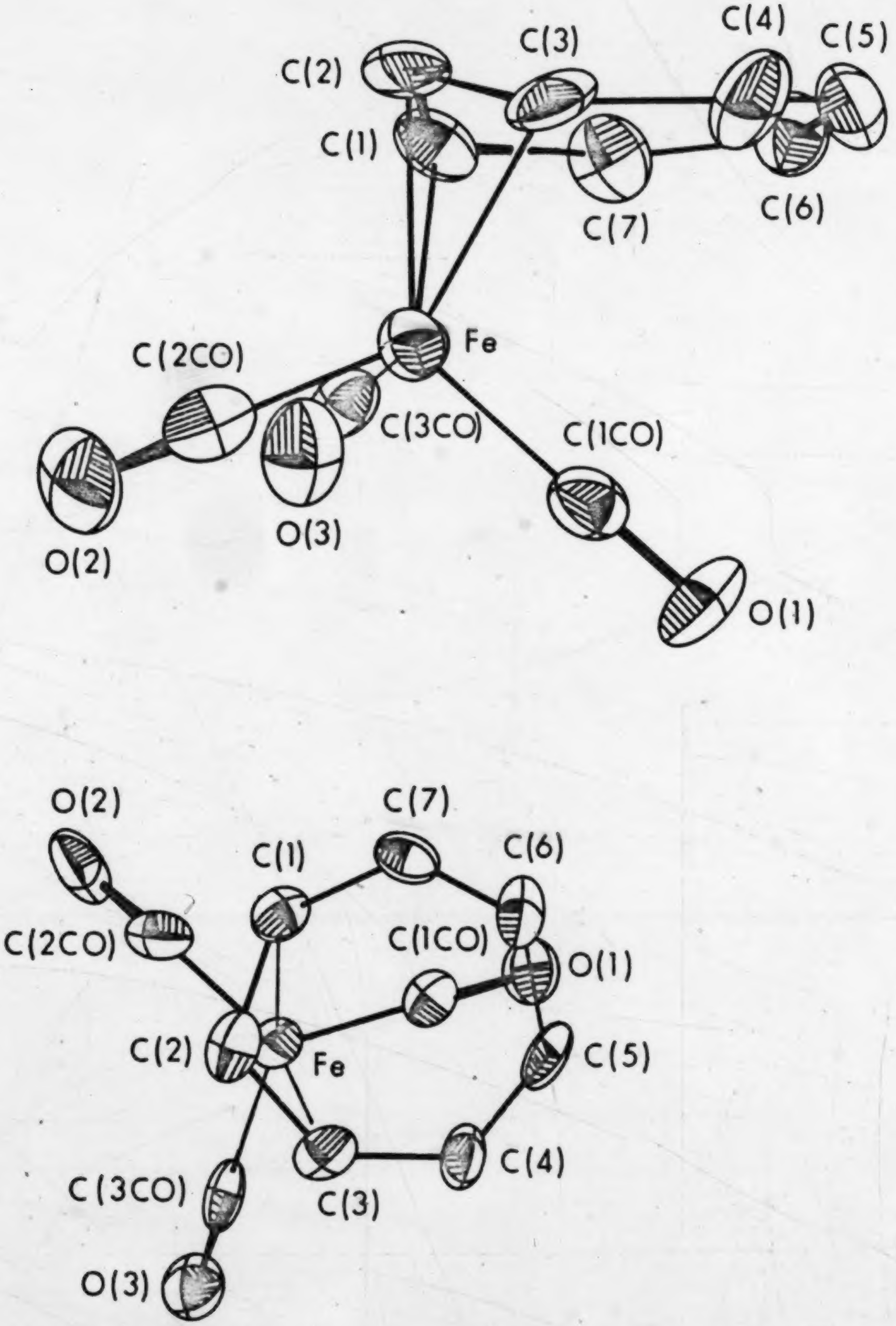

C(4)
C(5)
C(3)
C(2)
C(1)
C(7)
C(6)
Fe
C(2CO)
C(3CO)
C(1CO)
O(2)
O(3)
O(1)
O(2)
C(7)
C(1)
C(6)
C(2CO)
C(1CO)
O(1)
C(2)
Fe
C(5)
C(4)
C(3CO)
C(3)
O(3)

Figure XIV. Molecular structure of $[(C_7H_7)Fe(CO)_3]^-$.[107]

the relevant distances and angles are summarized in Table II.

TABLE II

Selected intramolecular distances (Å) for the anion $[(C_7H_7)Fe(CO)_3]^-$.[107]

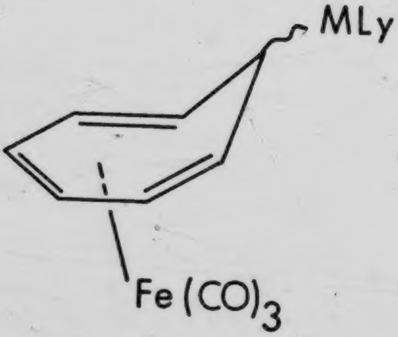
C(1)	-Fe	2.113(12)
C(2)	-Fe	1.983(10)
C(3)	-Fe	2.137(11)
C(1CO)	-Fe	1.766(12)
C(2CO)	-Fe	1.755(13)
C(3CO)	-Fe	1.780(13)
C(1)	-C(2)	1.432(21)
C(2)	-C(3)	1.412(22)
C(3)	-C(4)	1.421(24)
C(4)	-C(5)	1.344(23)
C(5)	-C(6)	1.428(24)
C(6)	-C(7)	1.305(25)
C(7)	-C(1)	1.429(22)

Figure XIV clearly shows the η^3-coordination, the bending of the uncoordinated diene fragment away from the iron center, the alternating carbon-carbon bond lengths in this unit and the staggered conformation of the carbonyl ligands with respect to the ring. The angle between the C(1), C(2), C(3) plane and the plane defined by the C(1), C(3), C(4), C(5), C(6), and C(7) carbon atoms is 31°, in reasonable agreement with the predicted value of 40°. We note that in a related highly fluxional molecule, $(\eta^4-C_8H_8)-Fe(CO)_3$, the dihedral angle between bound and free diene fragments is 41°.[9]

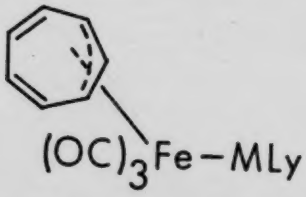
The low activation energy predicted for the "ring whizzing" in $[(C_7H_7)Fe(CO)_3]^-$ has also been indirectly verified by experimental observation. As shown in Figure X the protons of the cycloheptatrienyl ring in 16 appear as a single sharp line at $\delta = 4.90$ in the ^1H NMR spectra down to -110°C. Only at lower temperatures does the resonance broaden and disappears into the baseline at ~ -140°C. The chemical shift differences of the protons of the seven-membered ring in the static structure are most likely less than 5 ppm. Combining these shift differences with the low coalescence temperature (T_c<-140°C) observed for 16 we estimate that the free energy of activation for the rearrangement involved is less than 25 kJ mol^{-1}.

5. Scope of the present research.

In view of the interesting properties of $[(C_7H_7)-Fe(CO)_3]^-$ it was considered desirable to extend the known reactivity[55,105,112] of this anion towards electrophilic reagents. Two reaction products, 21 and 22 can be envisioned from the reaction of 16 with an electrophile. It was particularly interesting to speculate whether electrophilic reagents which lead exclusively to 21 or 22 could be found and whether a discrimination towards the final product as a function of the electrophiles employed could be achieved.



21



22

Few precedents for the formation of compounds of type **21** and **22** were known. The reaction of **16** with H^+ results in the formation of the parent molecule $(\eta^4\text{-}C_7H_8)Fe(CO)_3$[105] while the interaction of **16** with transition metal carbonyl halides results in cis-heterodinuclear cycloheptatrienyl complexes.[112] The compounds isolated in the latter reactions contain a metal-metal bond and can be classified as belonging to the class of compounds of type **22** although both metals are coordinated to the briding cycloheptatrienyl group. In order to extend the applicability of $[(C_7H_7)\text{-}Fe(CO)_3]^-$ as a starting material for novel organometallic molecules and to obtain further evidence for the above discrimination we started to investigate the reactivity of **16** towards electrophilic species of the type L_yMX in which L_yM symbolizes the central transition metal atom or main group element with its ancillary ligands and X is a halogen atom.

The properties of the reaction products $\underset{\sim}{21}$ and $\underset{\sim}{22}$ are also potentially interesting and would warrant further studies. The $(\eta^4\text{-}C_7H_7R)Fe(CO)_3$ compounds, for example could exhibit two different stereochemistries. Pauson and coworkers established the *exo* stereochemistry for the products of the interaction of a nucleophilic species with $[(C_7H_7)Cr(CO)_3]^+$.[88] In contrast Deganello suggests an 7-endo substitution in the reaction of $\underset{\sim}{16}$ with $[(C_7H_7)\text{-}M(CO)_3]^+$, M = Cr, Mo, W.[55] Our efforts therefore were directed towards establishing the stereochemistry of the anticipated $(\eta^4\text{-}7\text{-}C_7H_7ML_y)Fe(CO)_3$ complexes and to determine the feasibility of inducing an intramolecular migration of the ML_y group from carbon to iron should *endo* stereochemistry be found. An interesting aspect of these η^3- and η^4-compounds is their possible stereochemically nonrigid behaviour. The fluxionality of η^3-cycloheptatrienyl derivatives of the transition metals has been mentioned already in a previous section. Until recently however, unsubstituted $(C_7H_8)Fe(CO)_3$ was regarded as a rigid molecule as far as the movement of the $Fe(CO)_3$ moiety with respect to the ring is concerned. Only since the advance of the spin saturation transfer technique has it been shown[41c,d] that this compound too undergoes a temperature dependent rearrangement. The synthesis of substituted derivatives would not only make this process possibly more amenable to NMR studies but a better mechanistic understanding of the rearrangement would likely result as well.

During the course of this work other workers also communicated their findings on the reactivity of this anion,[55,107] while others commented upon the rearrangement mechanisms of its derivatives.[41c,d]

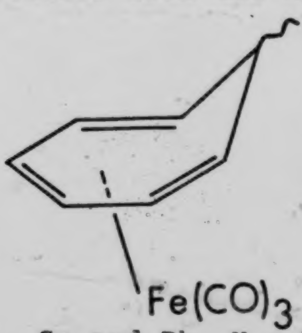
CHAPTER TWO

THE REACTIONS OF THE ANION $[(C_7H_7)Fe(CO)_3]^-$ WITH MAIN GROUP IV ELECTROPHILES.

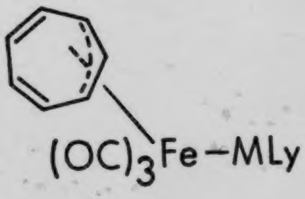
Introduction

As shown in Chapter I $[(C_7H_7)Fe(CO)_3]^-$ is an interesting and useful starting material for the synthesis of a variety of cycloheptatriene and cycloheptatrienyl based organometallic complexes. This chapter examines the reactivity of 16 towards main group IV electrophiles.

In accordance with the 18 electron rule, two structural isomers, 21 and 22, can be envisioned as the final reaction products from the interaction between 16 and R_3MX (M = Si, Ge, Sn and Pb, X = halogen, and R = alkyl or aryl). The viability of both types of reaction products stems from observations by other workers on the reactivity of 16. The interaction of this anion with D_2O,[105] with $[(\eta\text{-}C_7H_7)\text{-}M(CO)_3]^+$, M = Cr, Mo, and W,[55] and with ROC(O)Cl, R = Me, Et,[107] results in 7-substituted derivatives, 21, while the interaction of 16 with transition metal carbonyl halides leads to heterodimetallic cycloheptatrienyl complexes containing a metal-metal bond and are related to complexes



21



22

of type **22**.[112] Our search towards new synthetic routes to organometallic compounds led us to investigate the possibility of *selectively* preparing species of type **21** and **22**, that is, complexes which might be considered to be derived from forms **16a** and **16b**, respectively. It is important to point out here that compounds of type **21** and **22** could result from identical *initial* attack by the electrophile. Addition to either a ring carbon atom or to the iron atom followed by intramolecular migration can give rise to both **21** and **22**. An interesting recent example of the transfer of a nucleophile from the metal center to the C_7H_7 ring and subsequently back to the transition metal center is provided by the synthesis of $M(C_7H_7)(CO)_2I$ from $[M(C_7H_7)(CO)_3]^+$ (M = Mo, W).[84] In view of the decreasing M-C bond strength upon descending a main group family* one might anticipate a greater preference for complexes of type **22** in the order Pb > Sn > Ge > Si.

Finally we note that electrophilic attack on **16b**, the more stable bonding mode of **16**, could occur on either the iron atom or on the terminal allylic carbon atoms.** Therefore the observation of both types of products, **21** and **22** does not necessitate the presence of both bonding forms,

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*Although uncertainties remain it is apparent that the M-C (M = main group IV element) bond dissociation energies either decrease or remain constant on moving from M = Si to M = Sn. For a discussion see references 114 and 120.

**This aspect will be discussed in greater detail in a later chapter. See also reference 115.

16a and 16b, in solution. Such complexes could arise from 16b alone.

Results and discussion

Part A. Silicon and germanium derivatives

a. Synthetic Aspects.

Cycloheptatrienetricarbonyliron can be deprotonated by n-BuLi,[105] $Na[N(SiMe_3)_2]$,[107] NaOEt,[107] NaOMe,[105] t-BuOK.[55] We found that potassium hydride, if obtained from a freshly opened bottle, acts as an ideal deprotonating agent since the other product of the reaction, dihydrogen, evolves vigorously leaving behind only the anion 16 in solution.[116] However, slight impurities in KH seem to be sufficient in inhibiting its deprotonating action on $(C_7H_8)Fe(CO)_3$ (induction periods of up to hours have been observed before the first appearance of the characteristic red coloration of 16) and rendered this reagent unreliable for the preparation of 16. The ease of formation and the relative stability of the deep red air-sensitive anion $[(C_7H_7)Fe(CO)_3]^-$ at ambient temperature demonstrate the stabilizing effect of the coordinated $Fe(CO)_3$ unit upon the organic moiety.

As shown in Scheme IV the interaction of 16 with Me_3MX, M = Si, X = Cl, and M = Ge, X = Cl or Br,[*] and with Ph_3GeBr in THF at ambient temperature yields substituted cycloheptatrienetricarbonyliron complexes, i.e., compounds of type 21 ($SiMe_3$ = 21a, $GeMe_3$ = 21b, $GePh_3$ = 21c). The compounds were obtained as yellow crystalline solids which could be purified by sublimation, 21b, or crystallization

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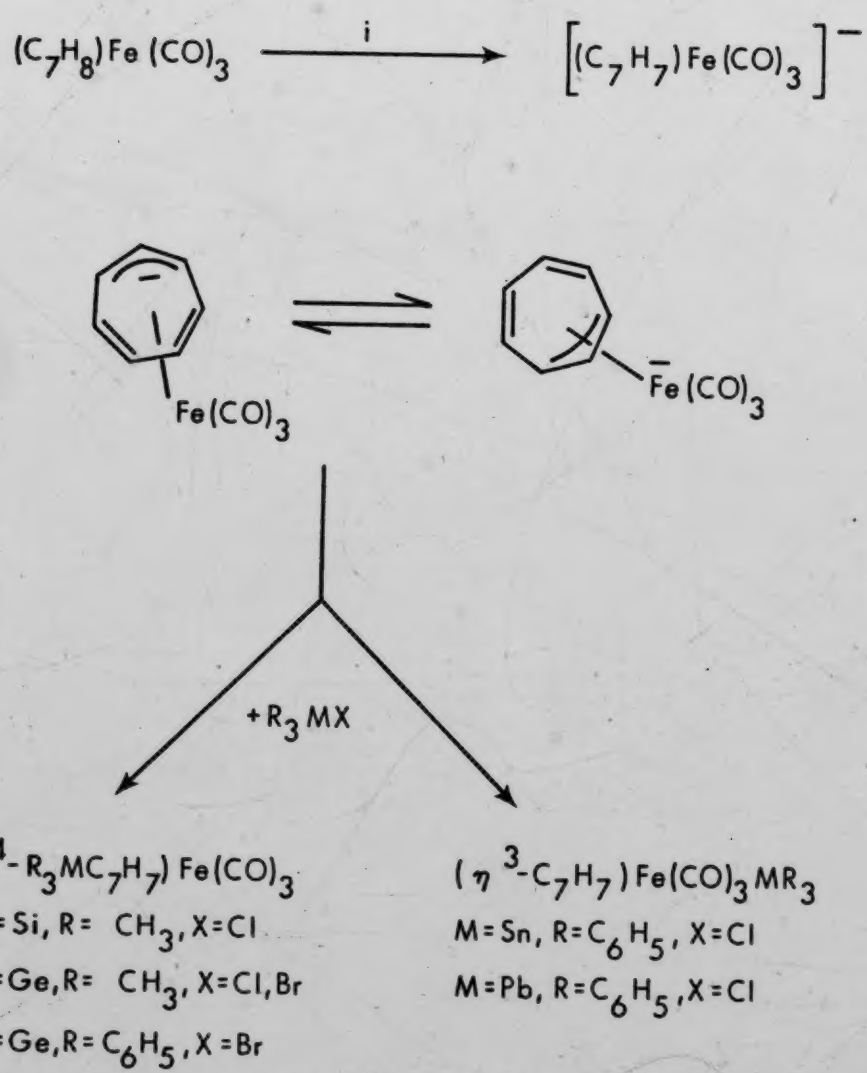
[*] Work on these derivatives in this research group was started by Mr. L.K.K. LiShingMan.


(C7H8)Fe(CO)3
i
[(C7H7)Fe(CO)3]−
Fe(CO)3
Fe(CO)3
+R3MX
(η4-R3MC7H7)Fe(CO)3
M=Si, R= CH3, X=Cl
M=Ge, R= CH3, X=Cl, Br
M=Ge, R=C6H5, X=Br
(η3-C7H7)Fe(CO)3MR3
M=Sn, R=C6H5, X=Cl
M=Pb, R=C6H5, X=Cl

i: n-BuLi / THF / -60°C
KH / THF / r.t.
t-BuOK / THF / r.t.

Scheme IV. The reactivity of $[(C_7H_7)Fe(CO)_3]^-$ towards main group IV electrophiles.

from hexane (21a, 21b, and 21c). Small amounts of the dimeric species $[(C_7H_7)Fe(CO)_3]_2$, 23, were observed in every reaction. This dimer, identified by ^1H NMR and infrared spectroscopy,[55] could be removed from the crude reaction mixture by chromatography on alumina, florisil, or silica gel, with hexane as eluent. The synthesis of 21c, however, proved to be more cumbersome. The presence of an additional impurity was deduced from the ^1H NMR spectra of the material obtained after the first crystallization. This spectrum showed a value of ~2.40 for the ratio of the phenyl resonances to the ring proton resonances, inconsistent with the expected value of 2.14 for 21c. Chromatography on any of the above column adsorbents with a variety of eluents with different polarities, e.g., hexane, THF, and dichloromethane, did not result in the separation of the two components. Only repeated fractional crystallization led to analytically pure 21c as shown by the proper experimental value of 2.14 for the phenyl to ring proton integration ratio and by elemental analysis. The second component was identified as $Ph_3GeOGePh_3$ by elemental analysis, ^1H NMR spectroscopy and mass spectrometry.

The complexes 21 were characterized by infrared, ^1H and ^{13}C NMR spectroscopy, by mass spectrometry, and by elemental analysis. The structure of one of the compounds, 21b, was also confirmed by crystallographic analysis. The compounds reported here are stable to air in the solid state for several hours and can be stored for long periods of time under an atmosphere of purified nitrogen. However, solutions of the complexes $\underset{\sim}{21}$ decompose rapidly upon exposure to air.

No reaction was observed upon the addition of $\underset{\sim}{16}$ to Ph_3SiCl and Me_3SiCH_2Cl, indicating a moderate nucleophilicity for $\underset{\sim}{16}$. Similar behaviour was observed by Graham and co-workers in the reactions of Ph_3SiCl with $[(C_7H_7)\text{-}Mo(CO)_2]^-$ [96b] and with $[(\eta\text{-}C_3H_5)Fe(CO)_3]^-$.[140] The reaction of Ph_3SiCl with $[Mn(CO)_5]^-$ also did not yield the anticipated product.[141]

The difficulties encountered in the reactions of $Mn(CO)_5^-$ with silicon halides have recently been described.[110] A less recent but detailed account of the anomalous behaviour of Ph_3SiCl towards transition metal anions is also available.[111] The rather limited reactivity of chlorotriphenylsilane towards transition metal carbonyl anions is probably due to the charge delocalization possible in the polar Ph_3SiCl molecule. Particularly if contrasted with chlorotrimethylsilane the reactivity of chlorotriphenylsilane towards metal carbonyl anions is therewith strongly reduced. $[(C_7H_7)Fe(CO)_3]^-$ also did not react with Me_3SiCH_2Cl. The stepwise substitution of Me_3Si for H in CH_3Cl reduces the electrophilicity of the resulting alkyl chlorides $(Me_3Si)_yCH_{3-y}Cl$. This together with the moderate nucleophilicity of anion 16 can explain the lack of reaction between these two species. Or, using a different approach we can conclude that the lack of reaction here once again classifies 16 as a moderate nucleophile. This is particularly evident if we contrast the above results to the data obtained from the reactions of substituted silylmethyl chlorides with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$, equation (16).[162]

$$\left.\begin{array}{l}[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-Na^+ + ClCH_2SiR_3 \longrightarrow \\ \qquad\qquad (\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2SiR_3 + NaCl \\ R_3 = Me_3,\ Me_2Ph,\ Me_2H.\end{array}\right\} \quad (16)$$

The high nucleophilicity of the cyclopentadienyliron dicarbonyl anion is well known[163] and the above reactions occur under mild conditions and in good yields (e.g. 82% for $R_3 = Me_3$).[162] Other trimethylsilylmethyl derivatives of the transition metals have been prepared by a similar route.[164] We note that often trimethylsilylmethyl iodide is used as the precursor.[164]

b. Mass spectral data.

The mass spectral data and major fragmentation patterns for the complexes 21 are summarized in Table III. The observed intensity ratios within each cluster agree well with those calculated using a locally available computer program.[159] The fragmentation pattern of each complex is

TABLE III

Mass spectra of the compounds $(R_3MC_7H_7)Fe(CO)_3$, and Major Fragmentation Processes for 21c.[a]

Assignment	21a[b]		21b[c]		21c[d]	
	m/e	rel. abund. (%)	m/e	rel. abund. (%)	m/e	rel. abund. (%)
parent$^+$	-	-	350	0.2	536[g]	<0.1
$P-R^+$	-	-	335	0.2	-	-
$P-CO^+$	276[e]	82.6	322	10.0	508	14.8
$P-CO-R^+$	-	-	307	0.3	-	-
$P-2CO^+$	248	35.4	294	4.6	480	14.2
$P-2CO-R^+$	-	-	279	0.2	-	-
$P-3CO^+$	220	100	266	19.4	452	100
$P-3CO-R^+$	-	-	251	7.5	-	-
$P-3CO-C_6H_6{}^+$	-	-	-	-	374	3.6
$P-3CO-2C_6H_6{}^+$	-	-	-	-	296	2.5
$C_7H_7MR_3{}^+$	164	11.6	210	0.3	396	0.3
$C_7H_7Fe^+$	147	68.4	147	100	147	99.9
$C_6H_6Fe^+$	134[f]	45.2	-	-	-	-
$C_5H_5Fe^+$	121[f]	15.2	-	-	-	-
$C_7H_7{}^+$	91	100	91	62.6	91	83.9
R_3M^+	73	93.5	119	4.1	305	52.6

continued...

TABLE III, Continued

Process	Metastable peaks Calcd.	Obs.
$(C_7H_7GePh_3)Fe(CO)_2^+ \longrightarrow (C_7H_7GePh_3)Fe(CO)^+ + CO$	453.5	452
$(C_7H_7GePh_3)Fe(CO)^+ \longrightarrow (C_7H_7GePh_3)Fe^+ + CO$	425.6	425.5
$(C_7H_7GePh_3)Fe^+ \longrightarrow C_{19}H_{16}GeFe^+ + C_6H_6$	309.5	309.0

---

[a] Not corrected for ^{13}C; all ions with m/e > 91 are shown. The nominal mass corresponding to the most abundant m/e-value within each cluster is reported.

[b] T = 110°C.

[c] T = 95°C.

[d] T = 140°C.

[e] Measured mass for this ion is 276.0254. The calculated mass for $C_{12}H_{16}O_2SiFe$ is 276.0269.

[f] These ions are characteristic of the breakdown of the $C_7H_7Fe^+$ group.[118] For a most recent guide to the decomposition of $C_7H_7^+$ in the mass spectrometer see reference 119.

[g] Determined by field ionization mass spectrometry.

dominated by the successive loss of three carbonyl groups from the parent molecular ion and, particularly for 21c, by the characteristic breakdown pattern of the R_3M substituent. Both of these processes have been identified before in organometallic complexes,[122,124] the loss of carbonyl ligands being the most fundamental fragmentation process in metal carbonyls and their derivatives. In all cases the ions $C_7H_7Fe^+$, $C_7H_7MR_3^+$, MR_3^+ and $C_7H_7^+$ are observed and belong to the more intense peaks. The facile cleavage of the M-C(ring) bond leading to the 6π-electron tropylium ion and a radical species, e.g. $\cdot MR_3$, also is not without precedent.[122,123,124] Although the spectra of the three compounds are very similar (e.g. one of the more intense peaks in each spectrum corresponds to $(C_7H_7MR_3)Fe^+$) one relevant difference between the complexes should be noted. While the compounds 21a and 21c show only fragmentation of the $C_7H_7MR_3$ group *after* the loss of *all* carbonyl ligands, complex 21b shows *simultaneous* loss of carbonyl and methyl groups, although, as expected, the former process is much preferred over the latter one. This can be understood in terms of the decrease in the M-C(sp^3) bond strength which occurs on going from Si (21a) to Ge (21b). Clearly the stronger Ge-C(sp^2) bond in 21c offsets this effect. The decrease in the M-C(sp^3) bond strength is also reflected in the relative abundances of the $C_7H_7MR_3^+$ peaks: 11.6% in 21a, the peak is only 0.3% in the complexes **21b** and **21c**.

Müller and co-workers have applied mass spectrometry to the determination of the position, *exo* or *endo*, of the substituent in 7-substituted cycloheptatrienetricarbonylchromium[122] and cyclopentadienylcycloheptatrienevanadium complexes.[123] It was found that in the *exo* isomers two competitive fragmentation processes were operating: (i) successive carbonyl losses from the parent molecular ion, and (ii) radical elimination of the *exo*-substituent to produce the stable $[(C_7H_7)Cr(CO)_3]^+$ where the positive charge is carried by the 6π-electron tropylium cation. On the other hand, in the *endo*- complexes fragmentation of the C_7H_7R moiety occurs only after the loss of all carbonyl ligands. Similar observations were made for (*exo*-6-R-cycloheptadienyl)$Mn(CO)_3$,[117] although in this instance, when R = H and CN, only decarbonylation of the molecular ion is observed. Unfortunately, it is not known whether the above correlation can be extended to the complexes **21**, especially in view of the fact that the special stabilizing influence of the 6π-electron tropylium cation is lost in these derivatives after the elimination of $R_3M\cdot$. $[(C_7H_7)Fe(CO)_3]^+$ is known[73] but it is a fluxional molecule in which only five carbon atoms of the C_7H_7 ring are coordinated to the iron center, forming a five-electron pentadienyl radical donor moiety. Thus, although the complexes **21** do not show the simultaneous loss of carbonyl ligands and $R_3M\cdot$ radical species, a deduction of *endo* stereochemistry for these compounds without supporting evidence would be premature at best. No ions due to species containing a direct Fe-M bond (i.e., FeM^+) could be detected; this supports the formulation of these complexes as belonging to the general class of compounds of type $\underset{\sim}{21}$.

c. Infrared spectral data

All three compounds show three carbonyl stretching frequencies in the range 2050 - 1950 cm^{-1}. Table IV shows a summary of these values together with the carbonyl stretching maxima of other tricarbonyliron complexes relevant to this study. The observed number of CO stretching maxima agrees with the low molecular symmetry determined for these complexes (*vide infra*). It is interesting to note that in accordance with the well-known electron donating ability of the MR_3 substituents[138] and the expected decrease in the electron accepting ability of the substituted $C_7H_7MR_3$ carbocycles, compared to the cycloheptatriene moiety, the carbonyl absorption bands in the compounds $\underset{\sim}{21}$ occur 7 - 10 cm^{-1} to lower frequencies than in the unsubstituted $(C_7H_8)Fe(CO)_3$.

The anomalously low C-H stretching frequency associated with an *exo* hydrogen on C(6) in a series of cyclohexadienyl complexes of the transition metals,[125] in the region

TABLE IV

Infrared Stretching Maxima[a] of the complexes $(C_7H_7MR_3)Fe(CO)_3$ and related compounds in the range 2060-1850 cm^{-1}.

Compound	Carbonyl Stretching Frequencies[a]			Solvent	Reference
$(7\text{-}Me_3SiC_7H_7)Fe(CO)_3$, **21a**	2044	1983	1969	cyclohexane	this work
$(7\text{-}Me_3GeC_7H_7)Fe(CO)_3$, **21b**	2043.5	1982.5	1968.0	cyclohexane	this work
$(7\text{-}Ph_3GeC_7H_7)Fe(CO)_3$, **21c**	2046	1978	1965	cyclohexane	this work
$(C_7H_8)Fe(CO)_3$, **2**	2050 2045	1989 1990	1975 1975	neat n-hexane	126 this work
$[(C_7H_7)Fe(CO)_3]_2$, **23**	2059	1990	1975	n-hexane	55
$[(C_7H_7)Fe(CO)_3]^-$, **16**[b]	1942	1868	-	THF	105, this work
$[(C_7H_7)Fe(CO)_3]^-$, **16**[c]	1949	1871	1851	acetone	107

[a] In cm^{-1}. [b] Li^+ or K^+ salt. [c] Na^+ salt.

2850 - 2700 cm^{-1}, is not observed for any one of the compounds 21, suggesting possibly *exo* stereochemistry of the MR_3 substituent at C(7).

d. NMR Spectral Data

The room temperature ^1H NMR spectral data of the complexes 21 are summarized in Table V. The spectra of 21b and 21c are also shown in Figure XV. The assignments of the resonances are indicated in the Figure and were obtained by homonuclear selective decoupling experiments.

The spectra demonstrate the well-known upfield shift of the outer protons of the coordinated diene fragment (protons H(1) and H(4)). The protons of the uncoordinated olefinic bond remain relatively unshifted compared to free cycloheptatriene. The spectra of all three compounds are very similar in appearance and also closely resemble the spectrum of $(\eta^4-C_7H_8)Fe(CO)_3$.[106] The presence of an η^4-coordinated cycloheptatriene ring in the complexes 21 is thus indicated. The approximately 1.2 ppm downfield shift of H(7) in the Ph_3Ge-substituted derivative with respect to the Me_3M analogues is surprising. Similarly, H(6) and H(1), the protons closest to the substituent, are shifted downfield by ~0.3 ppm. The chemical shift values of H(5) and one component of the overlapping H(2) and H(3) resonances remain constant while H(4) and the other component of the H(2)-H(3) resonance are slightly shifted upfield upon substituting Me_3Ge by Ph_3Ge. Both

TABLE V

^1H NMR chemical shift values[a] for the complexes $(R_3MC_7H_7)Fe(CO)_3$.

Compound	Assignment[b]							Solvent
	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	
21a	3.36	4.37 –	4.48	2.97	5.56	5.10	1.68	toluene
21b	3.41	4.34 –	4.59	2.96	5.51	5.02	1.81	toluene
21c	3.74	4.11 –	4.33	2.67	5.54	5.40	2.93	benzene
21c	3.75	4.06 –	4.42	2.80	5.56 –	5.26	2.94	toluene
2	2.89	4.59 –	4.74	2.72	5.68	5.03	1.89-2.12	benzene
1	5.28	6.12	6.55	6.55	6.12	5.28	2.20	toluene

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[a] Chemical shifts (δ) in ppm from TMS by appropriate conversion from internal solvent references.

[b] Multiplicities are shown in Figures XV and XVI while the coupling constants are discussed in the text.

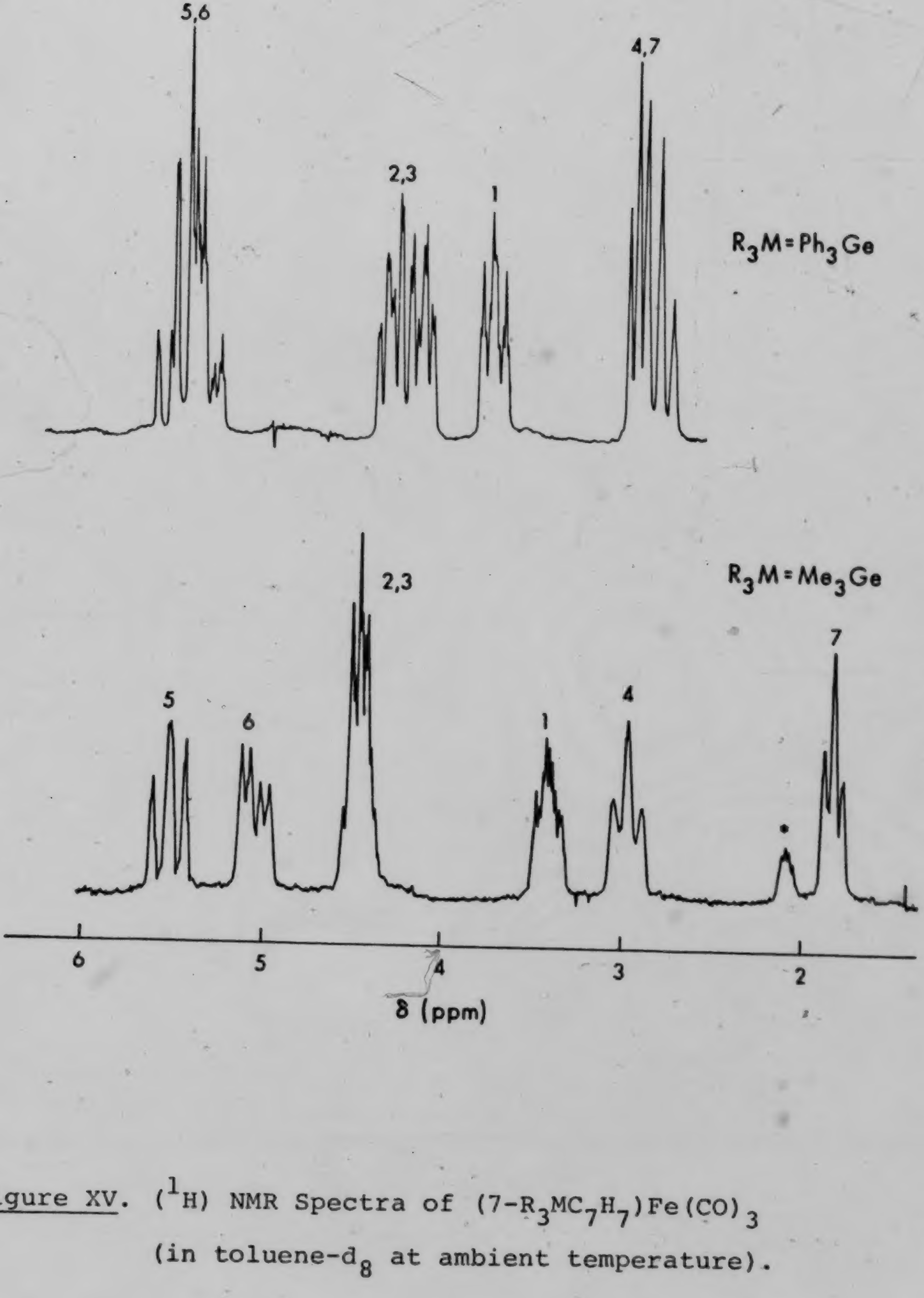

Figure XV. (^1H) NMR Spectra of $(7\text{-}R_3MC_7H_7)Fe(CO)_3$ (in toluene-d_8 at ambient temperature).

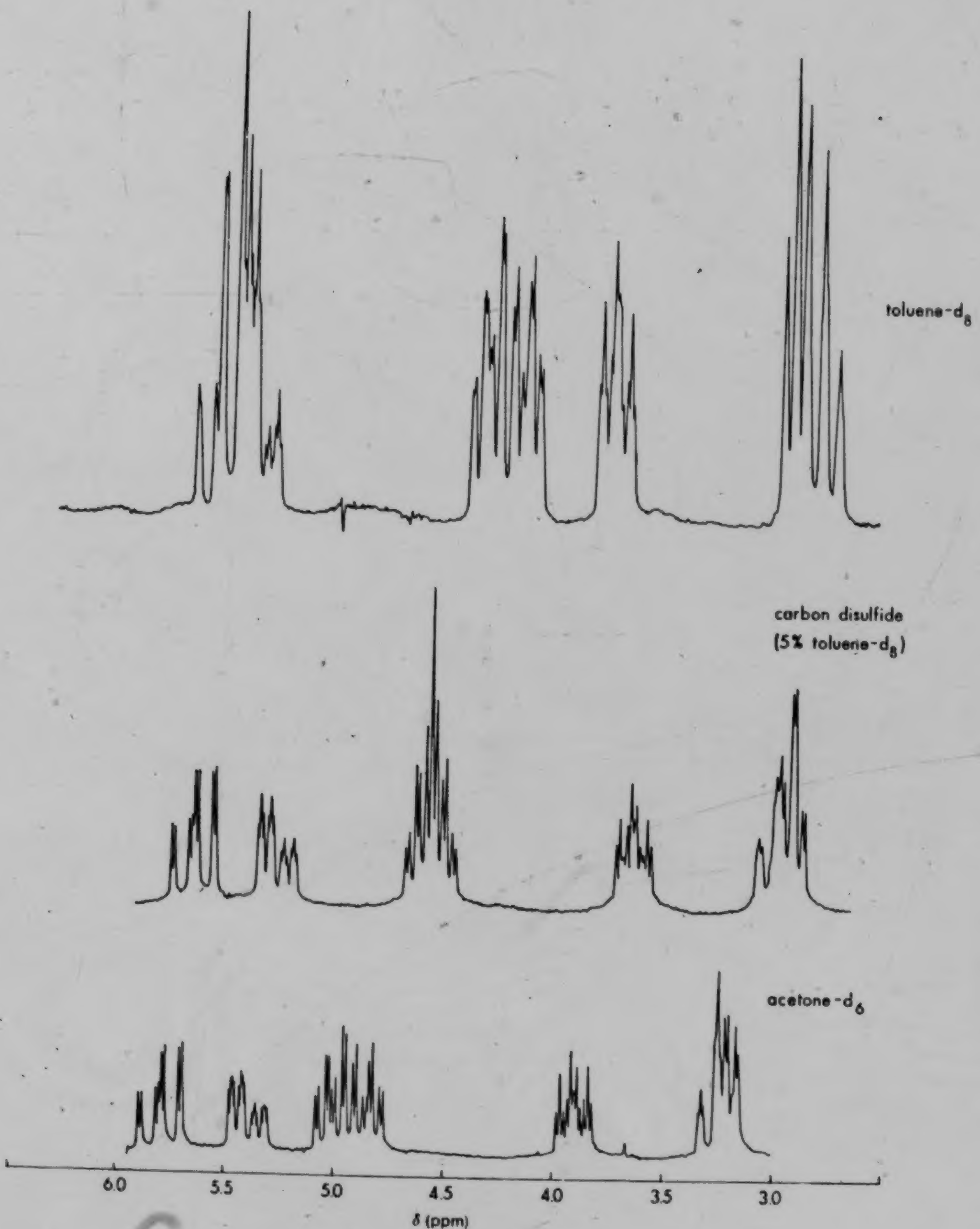

Figure XVI. ^1H NMR Spectra of $(7\text{-}(C_6H_5)_3GeC_7H_7)\text{-}Fe(CO)_3$ at ambient temperature.

the different inductive effect of the Ph_3Ge group and the presence of the magnetically anisotropic phenyl groups could possibly contribute to the observed shifts. Particularly the protons H(7), H(1) and H(6) experience the most pronounced effect due to their proximity to the substituent; the observed downfield shifts would indicate that these protons are positioned towards the deshielding region of the phenyl rings.

As shown in Figure XVI substantial solvent dependent shifts occur for 21c upon changing the polarity of the solvent. It was also observed that the chemical shift values of 21c are concentration dependent. Changes in the chemical shift values of some resonances can be as much as 0.7 ppm depending on the solvent and the concentration of the complex. It is clear that a comparison between the NMR spectra of these and related compounds should be made on the basis of data obtained in similar (better yet identical) solvents and compound concentrations.

The room temperature ^{13}C NMR spectra exhibit features similar to the proton nmr spectra. The large upfield shift of the C(1) and C(4) nuclei is evident while the uncomplexed carbon C(6) shows a small shift to lower field relative to free cycloheptatriene.[127] The ^{13}C NMR spectral data are summarized in Table VI. The assignments were obtained from heteronuclear selective decoupling experiments and by use of the spin saturation transfer

TABLE VI

^{13}C NMR chemical shift data for the complexes $(C_7H_7MR_3)Fe(CO)_3$.[a]

Compound	Assignment									Solvent
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	Ph	CO	Me	
21a	67.0	84.8	91.4	59.6	126.0	128.3	35.5	-	213.3	-2.5	toluene
21b	67.4	84.4	91.7	59.2	125.6	128.5	36.4	-	212.4	-2.6	n-decane
21c	65.8	85.4	91.8	58.6	b	b	36.2	127.0-136.4	212.5	-	toluene
2[c]	60.5	88.4	93.5	56.3	125.5	128.6	30.9	-	211.2	-	acetone/CS_2 (1/4.5)
1[d]	120.4	126.8	131.0	131.0	126.8	120.4	28.2	-	-	-	acetone/CS_2 (1/3)

[a] Chemical shifts (δ) in ppm from TMS by appropriate conversion from internal solvent references.

[b] The resonances due to C(5) and C(6) are obscured by the phenyl resonances in **21c**.

[c] This work, see also reference 113.

[d] This work, see also reference 127.

technique (*vide infra*). The observation of seven different carbon resonances and the similarity of the spectra to the spectrum of $(\eta^4\text{-}C_7H_8)Fe(CO)_3$ further corroborate the previous conclusion with regard to the bonding mode between the ring and the $Fe(CO)_3$ moiety.

A further potential utility of the NMR data is in the assignment of the stereochemistry of the substituent at the saturated carbon, C(7). The chemical shift values of the *exo*-7 and the *endo*-7 protons and the size of the vicinal coupling constants between H(7) and H(1), H(6) have been utilized most successfully in this regard.[88] In substituted $(\eta^6\text{-}C_7H_7R)Cr(CO)_3$ complexes the *exo* proton resonates, in the *endo* isomer, at δ ~1.85 ppm while the resonance of the *endo* proton in the *exo* isomer occurs at about 1-1.5 ppm to lower field (δ ~3.05) due to the lack of increased shielding by the unsaturated hydrocarbon ligand.[88] Based on this empirical rule we would conclude that whereas **21a** and **21b** have the *endo* stereochemistry, complex **21c** exists as the *exo* isomer. We think that it is highly unlikely that such a reversal of stereochemistry occurs in this series. Furthermore, the application of the above correlation to the present complexes is hampered by the effect of the substituents on the chemical shifts of H(7). It is known that the replacement of a hydrogen atom by the $SiMe_3$ [57] or the $SnPh_3$ [35b] moiety has a marked effect on the chemical shift value of the remaining hydrogen.

In $(C_7H_7)SiMe_3$ the remaining hydrogen resonance is shifted upfield by ~0.7 ppm while in $(C_7H_7)SnPh_3$ this resonance is shifted downfield by ~1.5 ppm. The inductive and anisotropic effects of the Ph_3Ge group on the proton chemical shifts have been commented upon before. Thus an unambiguous decision about the stereochemistry based on the chemical shift of H(7) cannot be made.

The values of the vicinal coupling constants between the 1,6- and 7-hydrogen atoms do not provide conclusive evidence about the stereochemistry at C(7) either. If the R_3M-group occupies the *exo* position relative to the $Fe(CO)_3$ moiety the dihedral angle between H(1) or H(6) and H(7) is rather small (<30°) and a large coupling constant (>6.5 Hz) between these hydrogens is expected according to the empirical Karplus curve.[128] However, if the substituent is positioned *endo* with respect to the metal a much larger dihedral angle (>120°) and a correspondingly smaller coupling constant (<3.0 Hz) between H(1), H(6) and the then pseudo-axial H(7) would result. A nice example of the applicability of this criterion is provided by $(C_7H_7)SnPh_3$.[35b,38] Arguments based on these values have also been utilized in $(C_7H_7R)Cr(CO)_3$ compounds.[88] The observed J-values for the complexes $\underset{\sim}{21}$ are: Me_3Si, 5.2 Hz, Me_3Ge, 5.0 Hz, and Ph_3Ge, 4.0 Hz, and again do not unambiguously indicate exo or endo stereochemistry.* Also the dependence of the coupling constants on factors other than the dihedral angle, such as ring size and hybridization, should not be neglected.[129] The stereochemistry around C(7) was therefore established by a crystallographic structure determination.

e. Structural Data.

The molecular structure of (*exo*-7-$Me_3GeC_7H_7$)Fe$(CO)_3$ was determined by X-ray diffraction.[143] A view of the structure is shown in Figure XVII while relevant molecular dimensions are given in Table VII. The η^4-coordination of the substituted cycloheptatriene ligand to the tricarbonyliron moiety is evident. It is also clear that the Me_3Ge substituent occupies the *exo*-7-position of the ring and the stereochemistry at C(7) is therewith established. The geometry of this complex bears a general resemblance to the tricarbonyliron complex of 7-phenylcycloheptatriene.[75] We presume that all complexes **21** have the same orientation of the substituent. This conclusion seems warranted in view of the apparent exo-attack on anion **16** and the similar spectroscopic characteristics of the complexes **21**.

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*The difficulty in assigning the correct stereochemistry at C(7) is emphasized by the chemical shift and J-values of **21c**: while the chemical shift data for H(7) (δ = 2.93 ppm) support *exo*-stereochemistry for the MR_3 group, the coupling constants rather indicate an *endo*-configuration.

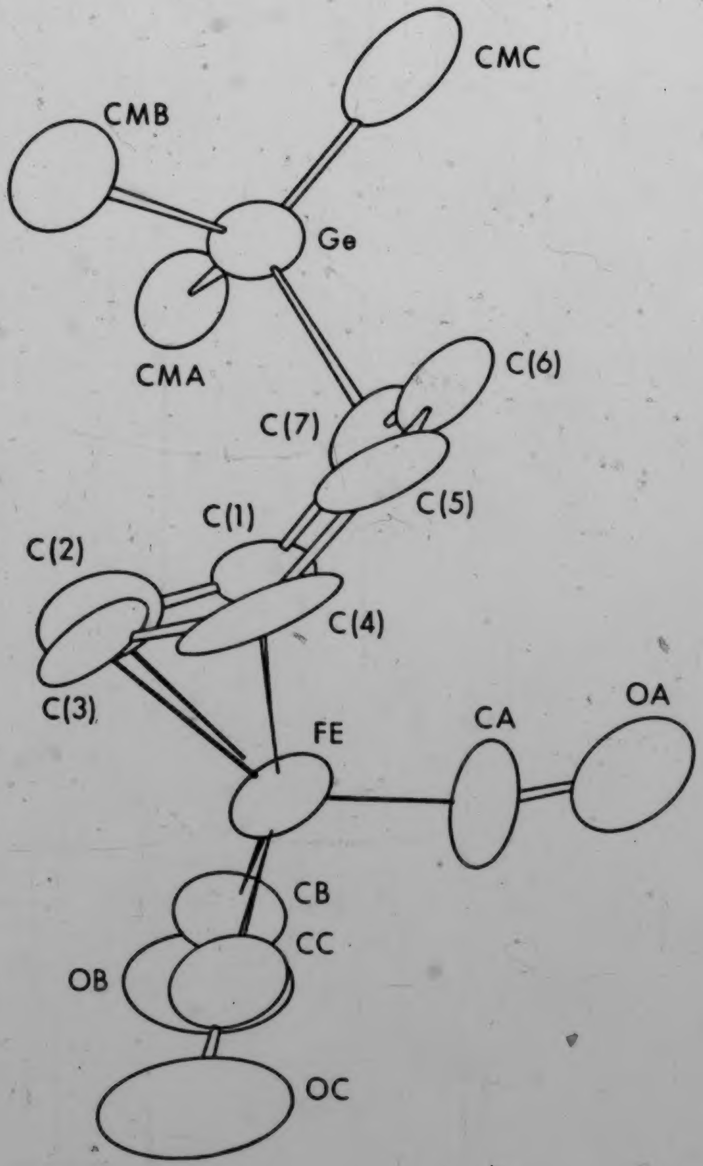

CMC
CMB
Ge
CMA
C(6)
C(7)
C(5)
C(1)
C(2)
C(4)
C(3)
FE
CA
OA
CB
CC
OB
OC

Figure XVII. Molecular structure of (*exo*-7-$Me_3GeC_7H_7$)-$Fe(CO)_3$.[143]

TABLE VII

Selected Intramolecular distances (Å) and angles for the compound $(\eta^4\text{-}C_7H_7Ge(CH_3)_3)Fe(CO)_3$.*

Distances		Angles	
C(1) - C(2)	1.489	CA - Fe - CB	102
C(2) - C(3)	1.463	CA - Fe - CC	101
C(3) - C(4)	1.489	CB - Fe - CC	88
C(4) - C(5)	1.397	C(1)- Fe - C(4)	80
C(5) - C(6)	1.394	C(2)- Fe - C(3)	41
C(6) - C(7)	1.512	Fe - CA - OA	166
C(1) - C(7)	1.542	Fe - CB - OB	177
Fe - C(1)	2.159	Fe - CC - OC	179
Fe - C(2)	2.122		
Fe - C(3)	2.078	C(1)-C(2)-C(3)	114
Fe - C(4)	2.162	C(2)-C(3)-C(4)	119
Fe - CA	1.627	C(4)-C(5)-C(6)	131
Fe - CB	1.845	C(5)-C(6)-C(7)	121
Fe - CC	1.796	C(1)-C(7)-C(6)	118
Ge - C(7)	2.008		

Plane	Atoms	
I	C(1), C(2), C(3), and C(4).	The four atoms comprising the plane are coplanar to within 0.004 Å with the Fe atom 1.636 Å below the plane
II	C(5), C(6), and C(7).	
III	C(1), C(4), C(5), C(6), and C(7).	The five atoms are planar to within 0.04 Å

Angles between planes :		
	I - II	148
	I - III	144
	II - III	4

---

*Preliminary Data

f. Stereochemical nonrigidity or the Performing Dogs in the Nighttime.

1. Variable Temperature ^1H and ^{13}C NMR Spectra.

In contrast to $(C_7H_8Fe(CO)_3$, the proton NMR spectra of which show no line broadening upon heating to 100°C, complexes $\underset{\sim}{21}$ show temperature dependent behaviour in their NMR spectra. As the temperature is raised the resonances due to H(1) through H(6) broaden, coalesce and reform into three new broad peaks at around 120°C. This is demonstrated in Figure XVIII which shows the ^1H NMR spectra of (*exo*-7-$C_7H_7GePh_3$)$Fe(CO)_3$ at 30° and 120°C. The corresponding spectra of the Me_3Ge analogue, $\underset{\sim}{21b}$, are shown in Figure XIX.[41a] It is clear that the resonance due to H(7) remains sharp over the entire temperature range and does not participate in the fluxional process. The positions of the three new peaks are in good agreement with the calculated averages from the low temperature chemical shift values of H(1) and H(6), H(2) and H(5), and H(3) and H(4), respectively. The observed line shape changes thus demonstrate that the molecules undergo an oscillatory motion of the $Fe(CO)_3$ unit such as to impart a time averaged mirror plane to the molecule. Hydrogen shifts, and no Me_3Si group migrations, could be observed for $\underset{\sim}{21a}$ and $\underset{\sim}{21b}$, the process being more facile for $\underset{\sim}{21a}$.[41a] The mechanisms and energetics of these rearrangements have not been further investigated. We note that with

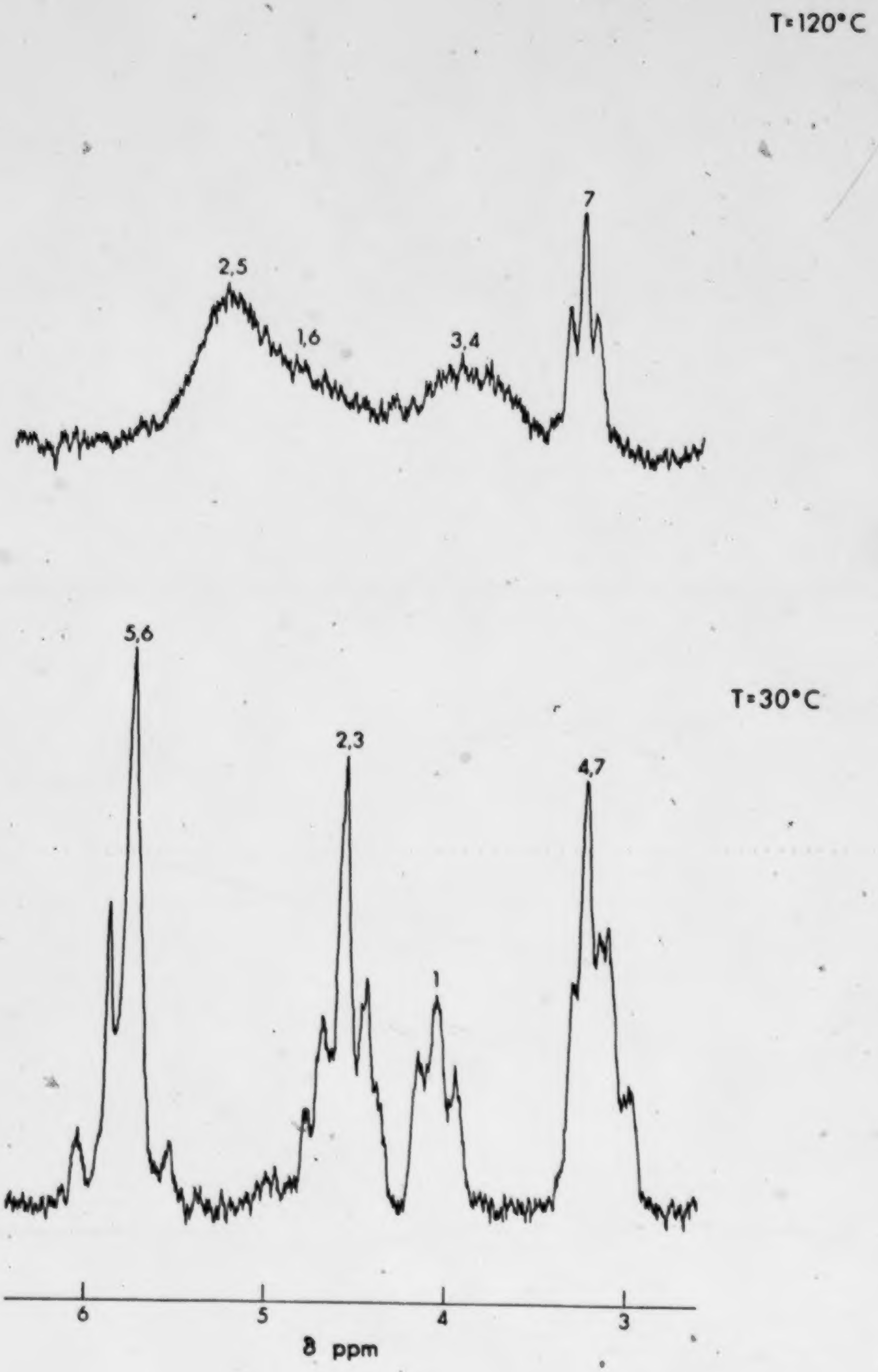


Figure XVIII. Variable Temperature 100 MHz ^{1}H NMR Spectra of $(\eta^{4}\text{-}7\text{-}Ph_{3}GeC_{7}H_{7})Fe(CO)_{3}$ in toluene-d_{8}.

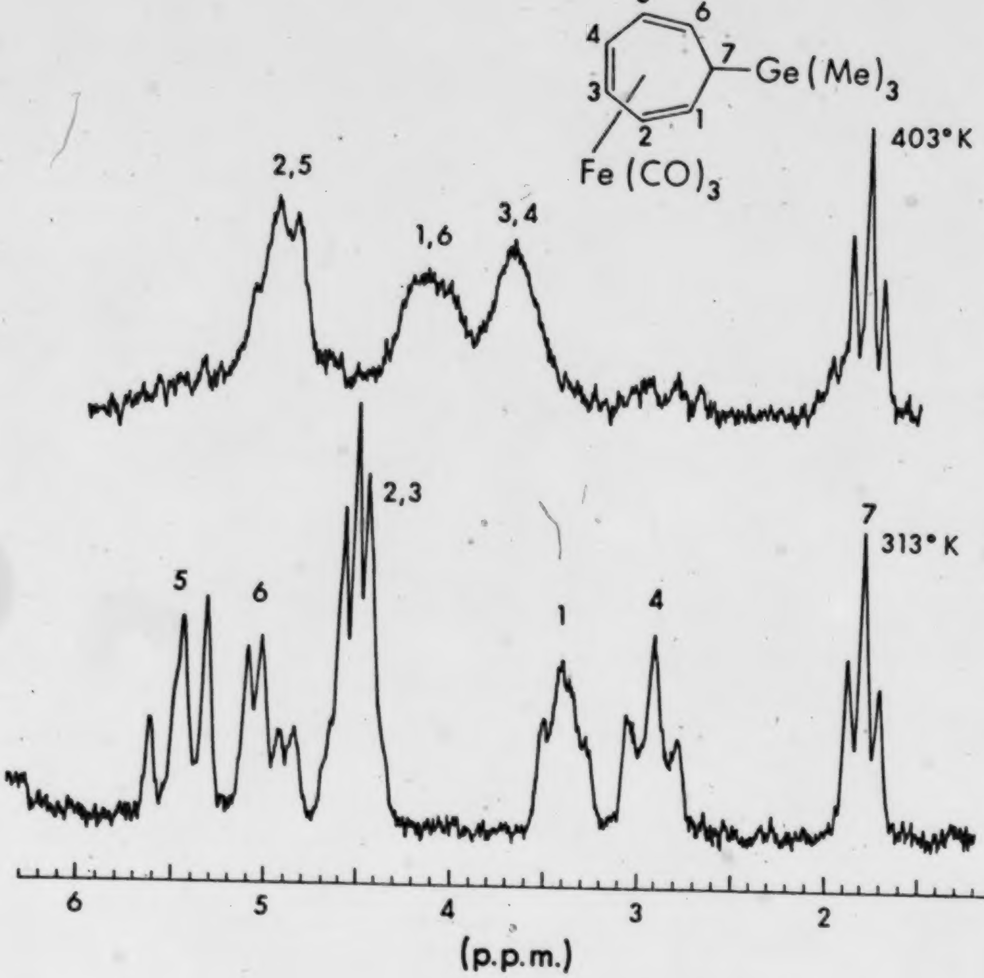


Figure XIX. Variable temperature 60 MHz ^{1}H NMR spectra of (η^4-7-Me$_3$GeC$_7$H$_7$)Fe(CO)$_3$ in diphenylether.[41a]

the metal free ligand, $(7\text{-}C_7H_7)SiMe_3$, hydrogen migration occurs in preference to Me_3Si group migration.[57] The migration in this case is known to proceed exclusively by a 1,5-hydrogen shift, Scheme II.

The proton decoupled variable temperature ^{13}C NMR spectra of 21c are shown in Figure XX. The ^{13}C NMR spectra exhibit similar temperature dependent behaviour. It is seen that the resonances due to C(1) through C(4) would coalesce into the baseline at a temperature slightly higher than 100°C. Due to the much larger chemical shift separations in the carbon-13 spectra, compared to the proton NMR spectra, the formation of the new averaged sets of resonances is not observed. That is, the high temperature limiting spectrum of 21c cannot be obtained (as substantial decomposition occurs at temperatures >120°C). Again the sharpness of the resonance attributed to C(7) over the entire temperature range is evident.

2. Energetics of the rearrangement process.

Coalescence Temperatures.

The coalescence temperatures (^1H (100 MHz) NMR) for the complexes 21 are tabulated in Table VIII together with the calculated $\Delta G^{\ddagger}$ values. The values obtained for T_c and $\Delta G^{\dagger}$ for each of the complexes 21 from the ^{13}C spectra are also shown in Table VIII. In each case $\Delta G^{\ddagger}$ was calculated using equation (6).[32,33] $\Delta\nu$ in these cases is the chemical shift difference in Hz between the two

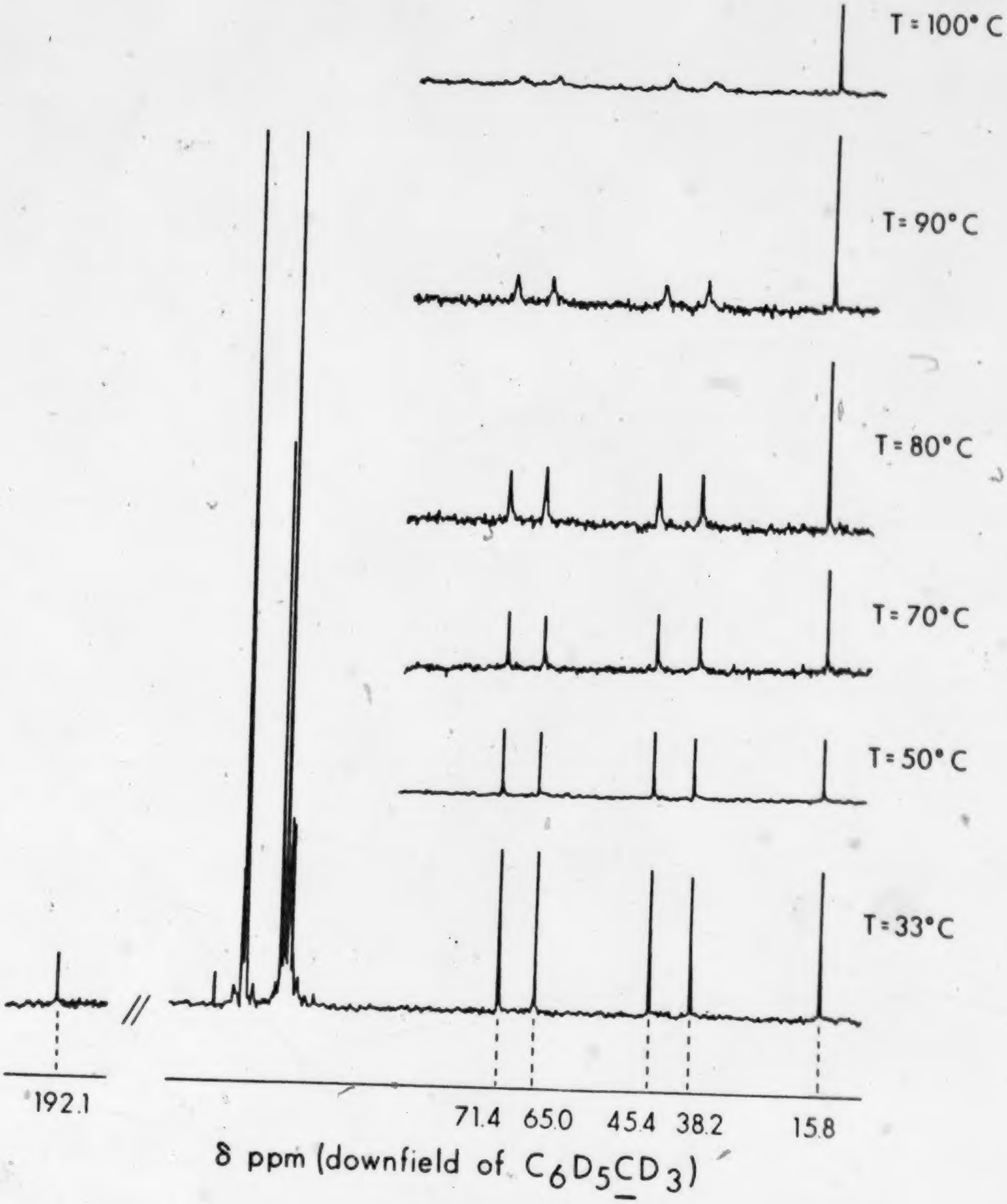


Figure XX. (^{13}C 15.08 MHz) Variable Temperature NMR Spectra of (7-$Ph_3GeC_7H_7$)Fe(CO)$_3$ in toluene-d_8.

TABLE VIII

Chemical shift differences,[a] coalescence temperatures,[b] and $\Delta G^{\ddagger}$ -values[c] for the complexes $(7\text{-}C_7H_7MR_3)Fe(CO)_3$.

Compound	^1H spectra			^{13}C spectra		
	$\Delta\nu$	T_c	$\Delta G^{\ddagger}$	$\Delta\nu$	T_c	$\Delta G^{\ddagger}$
21a	145	105	75	719	115	72
21b	150	95	73	735	127	74
21c	155	100	74	750	120	73

[a] In Hz.

[b] The chemical shift differences and temperatures quoted refer to the exchanging H(3)-H(4) and C(3)-C(4) pairs, respectively. T_c in °C, ±5°C.

[c] In kJ mol^{-1} at T_c, ±3 kJ mol^{-1}.

exchanging sites in the slow exchange limit, e.g., 100 x $\Delta\delta$ between H_1 and H_6, H_2 and H_5, and H_3 and H_4, at ambient temperature.

Determination of $\Delta G^{\ddagger}$ for (*exo*-7-$C_7H_7GePh_3$)$Fe(CO)_3$ by the spin saturation transfer technique.

The Forsén-Hoffman method provides an useful technique for determining the activation parameters of thermally labile complexes. The ^{13}C high temperature limiting spectrum of **21c** could not be obtained as substantial decomposition occurred at temperatures above 120°C. The Forsén-Hoffman or spin saturation transfer technique however enables one to obtain the desired activation parameters at the *onset* of chemical exchange, i.e., at temperatures where only slow exchange is occurring ($.005 \leqslant k \leqslant 5\ sec^{-1}$).[25,31,136] As such the method forms an invaluable addition to the conventional line shape technique. Furthermore, the method constitutes a convenient way of labelling specific nuclei. In our case this proved to be effective in confirming the initial assignment of the carbon atoms C(2) and C(3) by selective proton decoupling experiments. Due the the very similar chemical shift values of the protons H(2) and H(3) only a tentative assignment for C(2) and C(3) could be made. The selective irradiation of carbon atom C(4) of **21c** at 50°C results in a drastic decrease in the intensity of the resonance tentatively assigned to C(3), therewith establishing C(3) and C(4) as a pair of exchanging carbon atoms and thus confirming the resonance at δ = 91.8 ppm to be due to C(3).

Quantitative information about the magnitude of the activation parameters for the rearrangement in 21c could be obtained by selectively irradiating the resonance due to C(4) at various temperatures in the range 35-65°C thereby avoiding any complications due to the decomposition of this compound at elevated temperatures. By measuring the equilibrium magnetization of carbon atom C(3), $M_z^{C(3)}(\infty)$, in the presence of saturation at C(4) the lifetime at C(3) can be calculated using equation (17),[25,136]

$$\tau_{C(3)} = \frac{M_z^{C(3)}(\infty)}{M_z^{C(3)}(0) - M_z^{C(3)}(\infty)}\; T_1^{C(3)} \tag{17}$$

where $M_z^{C(3)}(0)$ is the normal equilibrium magnetization of carbon C(3) in the absence of irradiation at C(4). $T_1^{C(3)}$ is the spin-lattice relaxation time of atom C(3) and is measured by the $(180-\tau-90-(\text{sample})-T)_n$ pulse sequence with $T \geqslant 5T_1$. $T_1^{C(3)}$ and $T_1^{C(4)}$ are comparable at all temperatures.[25] The rate of leaving one site, e.g. C(3), is given in equation (18).

$$\frac{1}{\tau_{C(3)}} = \frac{M_z^{C(3)}(0) - M_z^{C(3)}(\infty)}{\left[M_z^{C(3)}(\infty)\right]\; T_1^{C(3)}} = \left[\frac{M_z^{C(3)}(0)}{M_z^{C(3)}(\infty)} - 1\right]\frac{1}{T_1^{C(3)}} \tag{18}$$

Experimentally $M_z^{C(3)}(0)/M_z^{C(3)}(\infty)$ is determined by comparing the signal area of the C(3) peak without and with saturation of carbon atom C(4). In the present case the heights of the ^{13}C signals were taken as a measure of $M_z^{C(3)}(t)$.[136] With the exchange rate k being equal to $\tau_{c_3}^{-1}$ the free energy of activation can be extracted from a plot of ln(k/T) vs. 1/T.

$$\ln(k/T) = 23.760 + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} \tag{19}$$

intercept yields: $23.760 + \frac{\Delta S^{\ddagger}}{R}$

slope yields: $-\frac{\Delta H^{\ddagger}}{R}$

Figure XXI shows the determination of the spin-lattice relaxation time of the carbon atoms C(1) through C(4) and C(7) at 30°C. T_1-values were determined at different temperatures and subsequently plotted as a function of the temperature, Figure XXII. A straight line resulted and intermediate values of T_1 were obtained from this graph. The Forsen-Hoffman experiment is demonstrated in Figure XXIII while the obtained values at various temperatures for $M_z^{C(3)}(\infty)/(M_z^{C(3)}(0)-M_z^{C(3)}(\infty))$, $T_1^{C(3)}$, and k are summarized in Table IX. A plot of ln(k/T) vs. 1/T is shown in Figure XXIV. Three independent spin saturation transfer experiments were performed and identical results were observed. The values obtained for $\Delta H^{\ddagger}$, 84 kJ mol^{-1}, and $\Delta S^{\ddagger}$, 18 Jk^{-1} mol^{-1} lead to a value of 77 kJ mol^{-1} for $\Delta G^{\ddagger}_{T_c}$ which compares well with the parameters extracted from the approximate expressions which apply at the coalescence temperatures (74 kJ mol^{-1}).

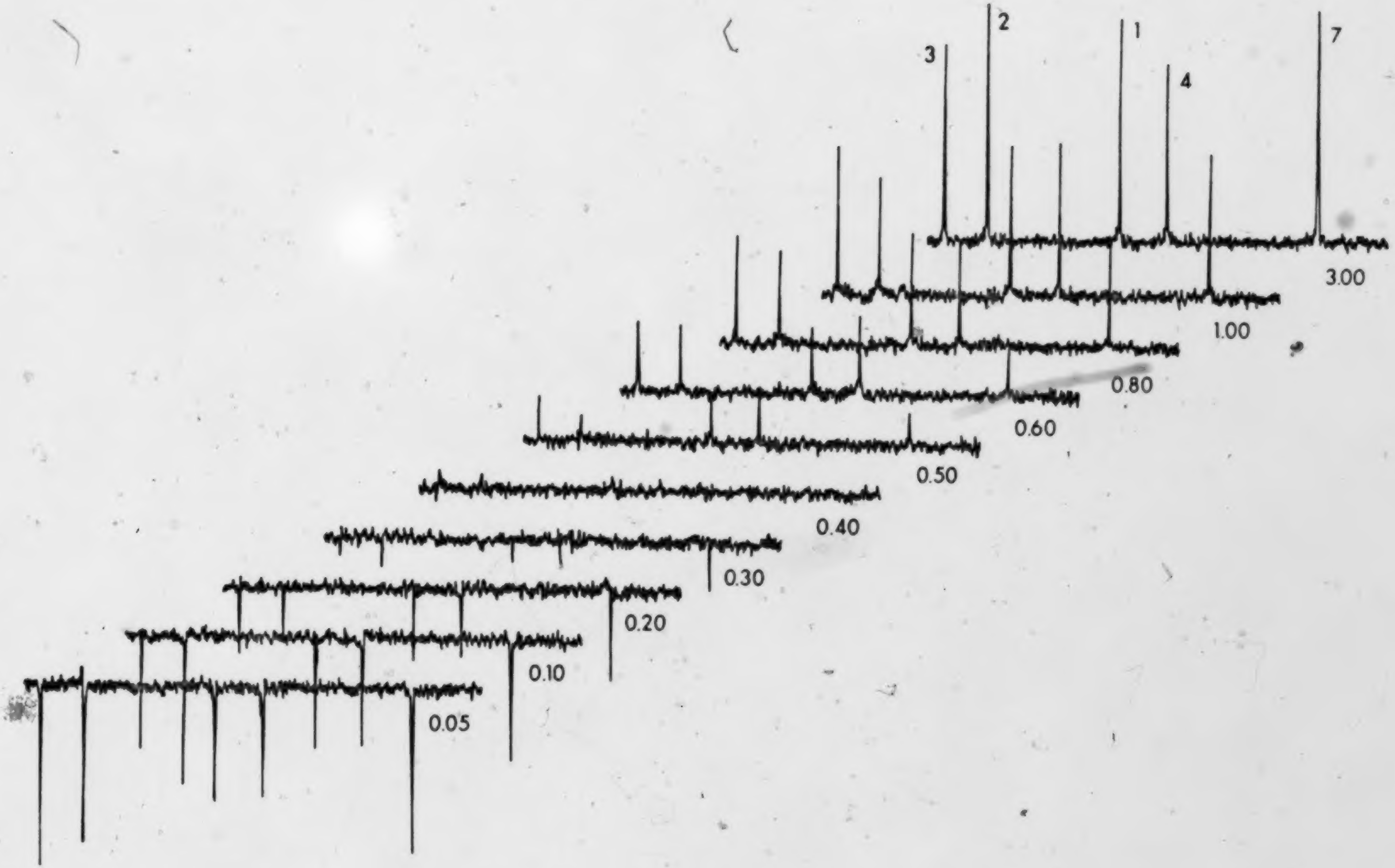


Figure XXI. Determination of the longitudinal relaxation time (T_1) of the ring carbon atoms 1, 2, 3, 4, and 7 of $((C_6H_5)_3GeC_7H_7)Fe(CO)_3$. (30°C, 5.95×10^{-4} M in toluene-d_8).

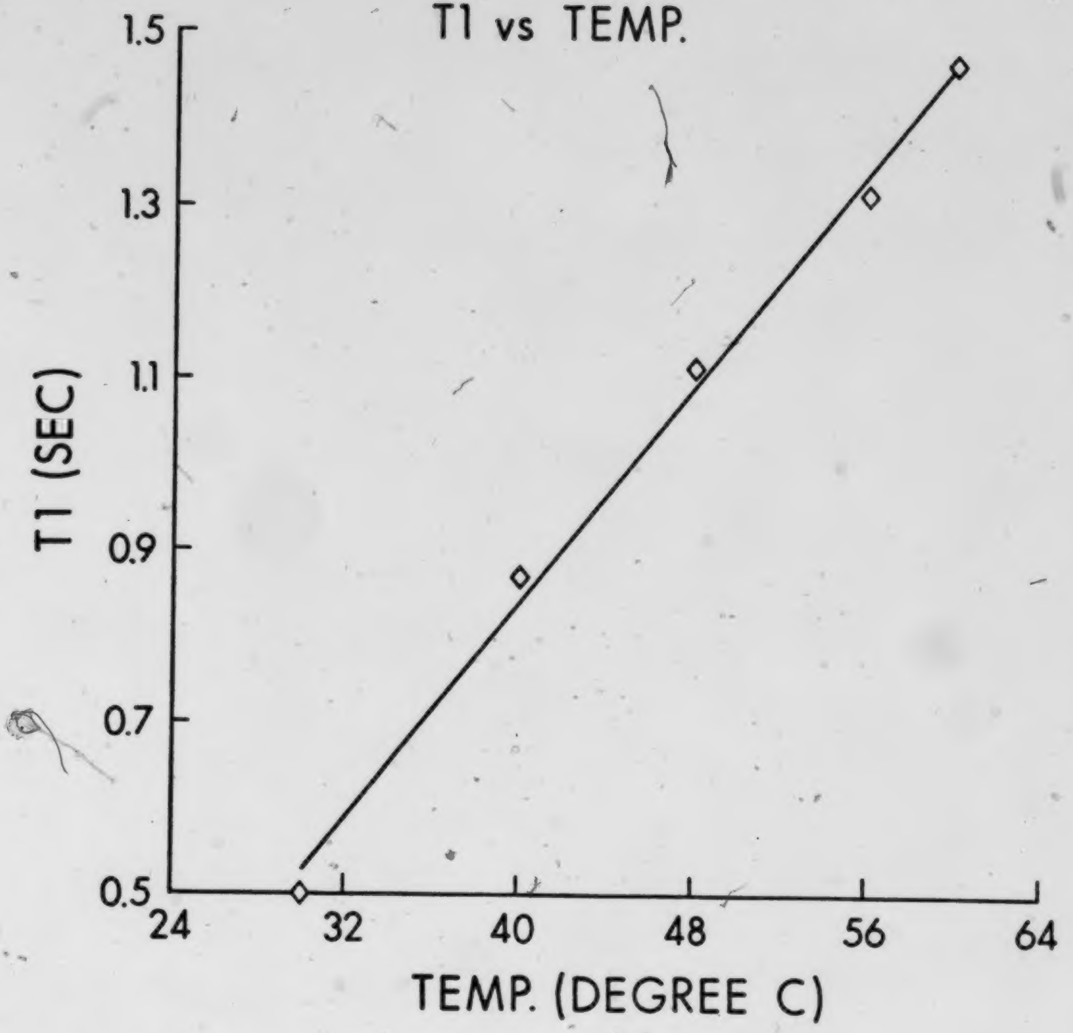


Figure XXII. Temperature dependence of the longitudinal relaxation time of carbon atom C-4 in $((C_6H_5)_3GeC_7H_7)Fe(CO)_3$.

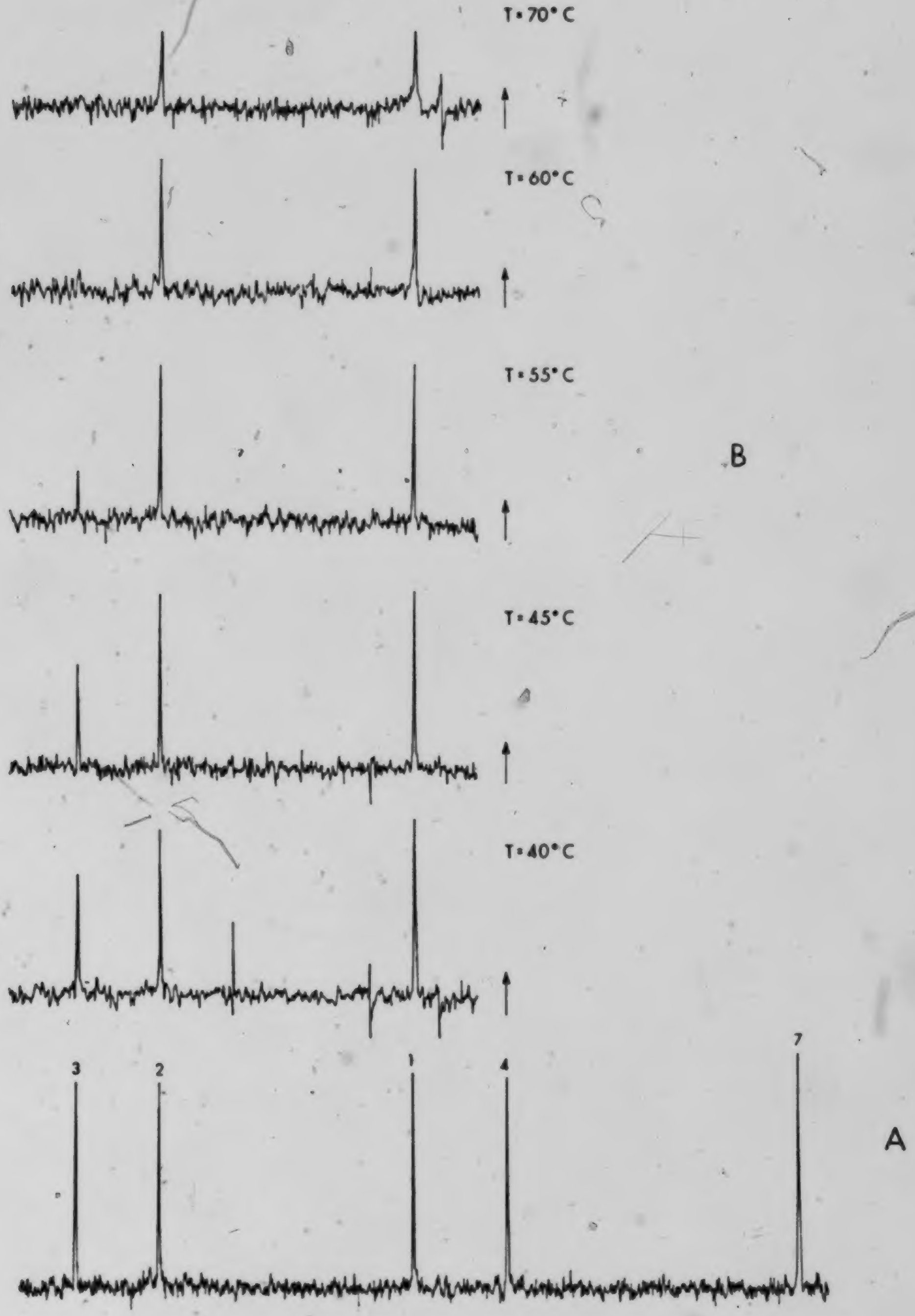


Figure XXIII. The Forsén-Hoffman spin saturation method as applied to $(Ph_3GeC_7H_7)Fe(CO)_3$.

A. ^{13}C NMR spectrum at 50°C showing the assignment of the signals.

B. ^{13}C NMR spectrum at different temperatures with an irradiating field applied at C(4).

TABLE IX

Spin saturation transfer data, rate constants and the free energy of activation for the complex (*exo*-7-$C_7H_7GePh_3)Fe(CO)_3$.

T, °C	T_1 of C_3, sec	$\frac{M_z(\infty)}{M_z(0)-M_z(\infty)}$ for carbon atom C_3	k, sec
40	0.868	2.69	0.428
45	0.994	1.44	0.699
55	1.309	0.44	1.754
60	1.462	0.20	3.367

At T = 120°C, $\Delta H^{\ddagger}$ = 84 kJ mol^{-1}, $\Delta S^{\ddagger}$ = 18 JK^{-1} mol^{-1}, and $\Delta G^{\ddagger}$ = 77 kJ mol^{-1}.

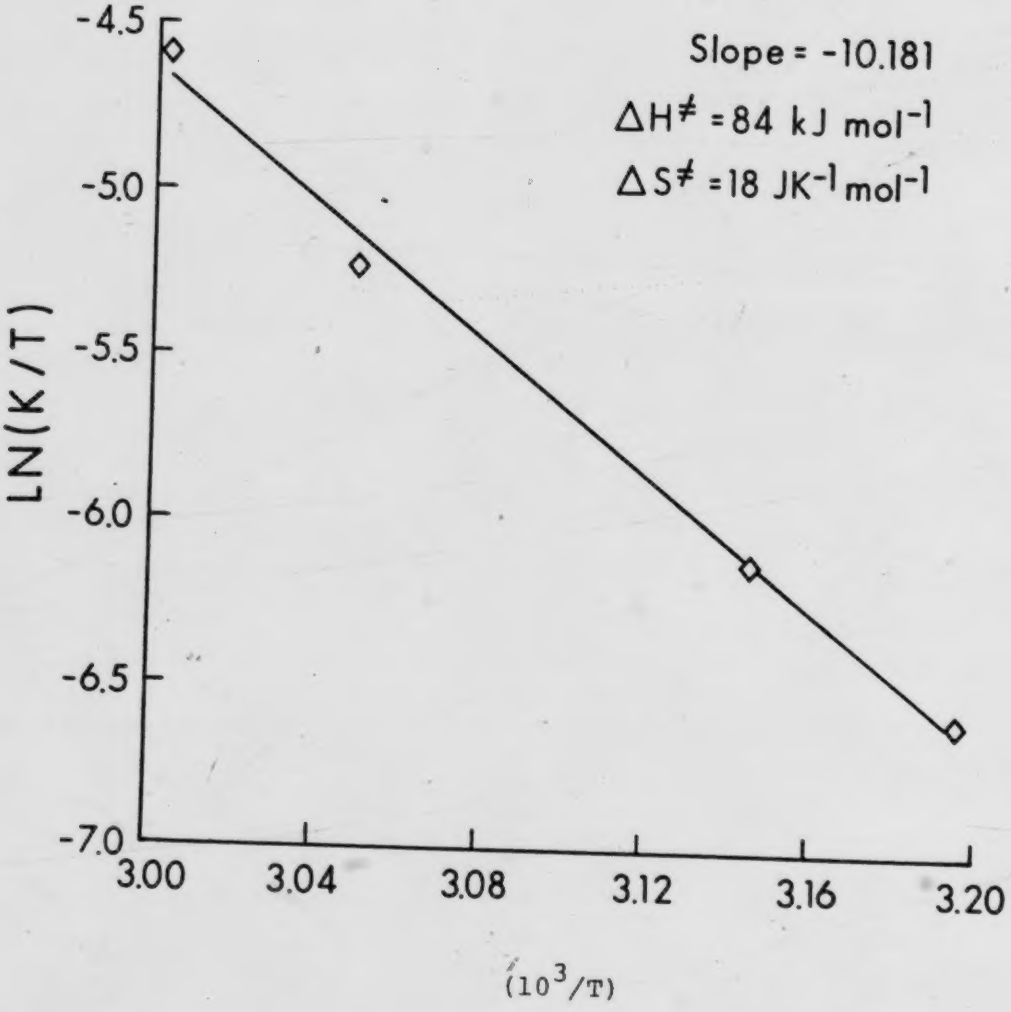


Figure XXIV. Plot of ln(rate/T) versus $10^3/T$ for the Forsén-Hoffman experiment on $((C_6H_5)_3GeC_7H_7)$-$Fe(CO)_3$.

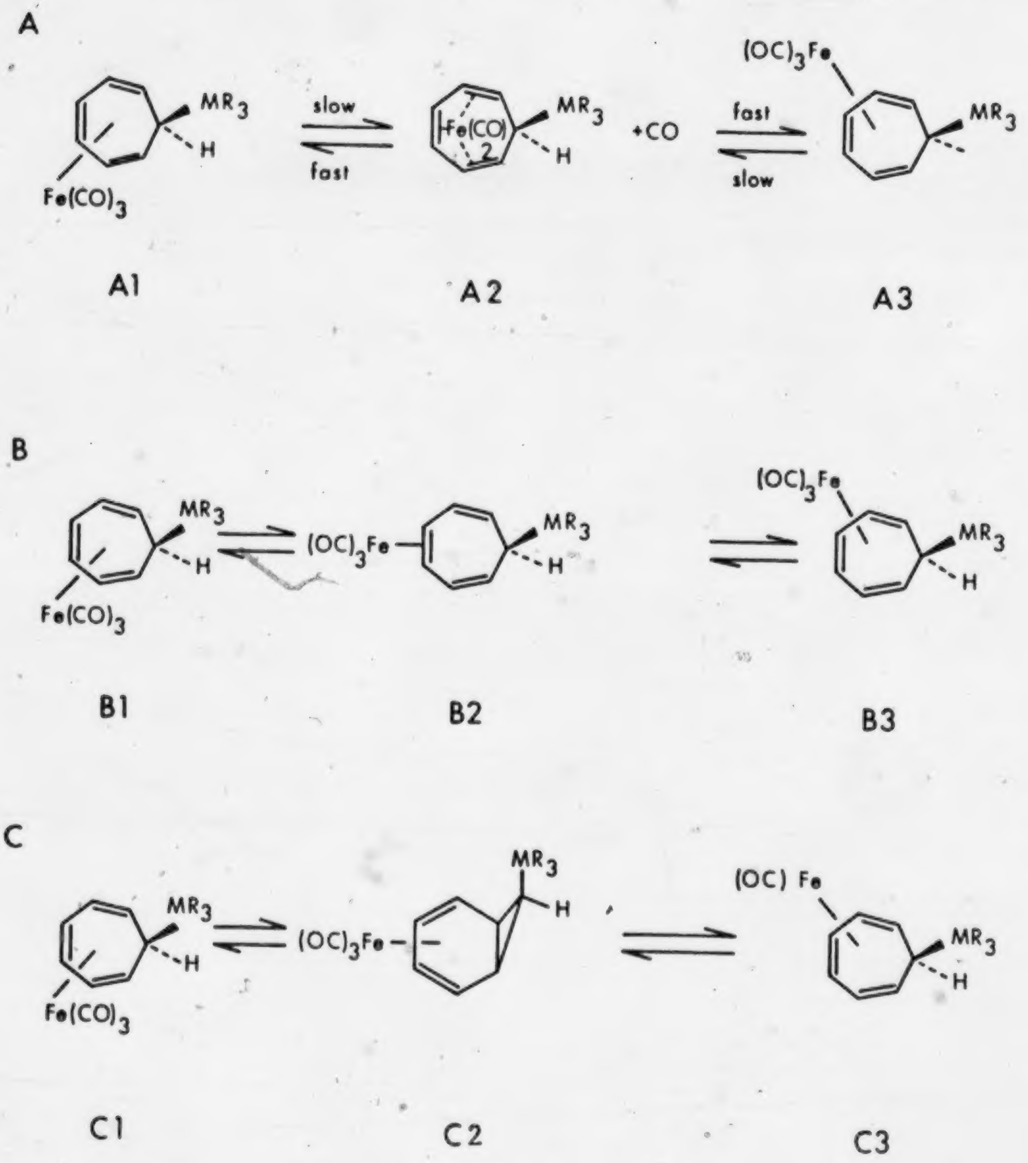
The remarkable lowering of the $\Delta G^{\ddagger}$ - values in these complexes compared to the unsubstituted parent compound $(C_7H_8)Fe(CO)_3$, $\Delta G^{\ddagger} \simeq 96$ kJ mol^{-1} should be noted.

3. Mechanism of the rearrangement process.

The observed temperature dependent ^{1}H and ^{13}C line shapes and especially the unchanging H(7) and C(7) resonances, indicating non-participation of these atoms in the rearrangement process, permit the elimination of hydrogen and MR_3 group migrations as being responsible for the nonrigid behaviour of the complexes 21. Indeed both of these processes would effect the line shapes of the H(7) and C(7) signals and the latter process would average the environment of all hydrogen and carbon atoms and would give rise to a single peak in the NMR spectrum. Selective *endo* hydrogen migrations have however been observed in *exo*-7-(^{2}H)-cycloheptatrienetricarbonyliron,[106,131] and also for 21a and 21b. These hydrogen migrations result in a mixture of isomers, quite contradictory to the process being considered here.

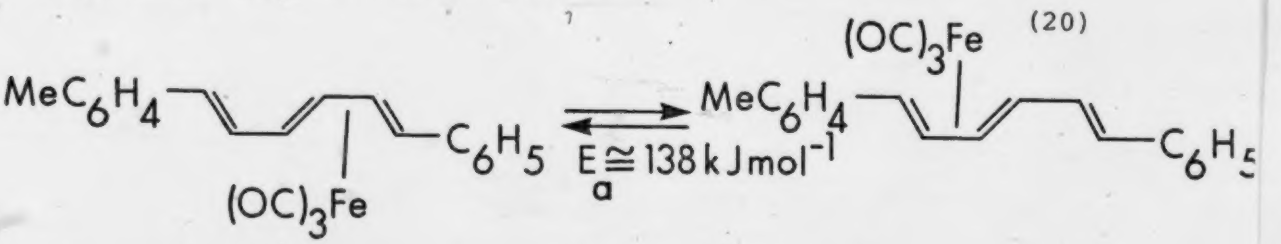
We can think of three other processes to explain the observed temperature dependence of the NMR spectra and these are depicted in Scheme V.

Process A involves the reversible dissociation of carbon monoxide with the simultaneous formation of a $(\eta^6-C_7H_7R)Fe(CO)_2$ intermediate. This short-lived species A2 then recombines with CO to form A3. The reported


A
MR3
H
Fe(CO)3
slow
fast
Fe(CO)2
+CO
fast
slow
(OC)3Fe
A1
A2
A3
B
(OC)3Fe
B1
B2
B3
C
(OC)3Fe
(OC) Fe
C1
C2
C3

Scheme V. Possible mechanisms for the rearrangement process in the compounds $(\eta^4\text{-}R_3MC_7H_7)Fe(CO)_3$.

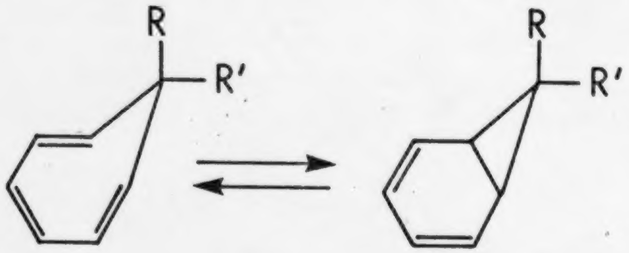
isolation of $(\eta^6\text{-}C_7H_8)Ru(CO)_2$ gives support for the consideration of this process.[71] The second feasible process, path B, involves a dechelation step of the $Fe(CO)_3$ moiety leading to the formation of the 16 electron intermediate B2 which contains an η^2-bound cycloheptatriene ring and would constitute an apparent 1,3 shift. Process C, involving two successive 1,2 shifts and the intermediacy of the bicyclo-(4,1,0)-heptadiene-1,3 structure, C2, also has the effect of a net 1,3 iron shift. Of course, process C could constitute a direct 1,3 shift without the intermediacy of the possibly high energy norcaradiene structure as well. The high energies generally involved in the dechelation of a double bond in $(diene)Fe(CO)_3$ complexes tend to disfavor process B. Whitlock has found that the energy of activation for a 1,3 shift in an acyclic system, equation (20), is 138 kJ mol^{-1}.[132]


(20)

Although the rearrangement must occur via an η^2 intermediate in the acyclic derivatives it is uncertain whether these complexes constitute an acceptable model for the cyclic cycloheptatriene derivatives. Nevertheless, the very high value of E_a observed for the dechelation process seems to argue against a dechelation pathway for the compounds considered here. Furthermore, this mechanism does not present a comforting explanation for the drastic difference in the $\Delta G^{\ddagger}$-values of $(C_7H_8)Fe(CO)_3$ (~96 kJ mol^{-1}) and the complexes 21 (~73 kJ mol^{-1}).

To distinguish between the processes A and C we attempted to enrich each of the compounds 21 with ^{13}CO. Prolonged heating in refluxing toluene under an atmosphere of labeled carbon monoxide however did *not* result in ^{13}CO incorporation as found by infrared spectroscopy and mass spectrometry. This then rules out process A as a dominant pathway. Process C thus appears to represent the most probable mechanism by which the nonrigidity of the complexes 21 manifests itself.

The lowering of the activation parameters for the present compounds could be taken as supporting the norcaradiene mechanism. The stability of the intermediate C2 is rather sensitive to substitution on C(7).[133] The magnitude of the substituent effects observed here is quite surprising and demonstrates the substantial influence a C(7)-group can exert on the free energy of activation for this rearrangement process. Electron accepting groups are known to shift the cycloheptatriene-norcaradiene equilibrium to the right, equation (21).[134,135,137] It has been shown



(21)

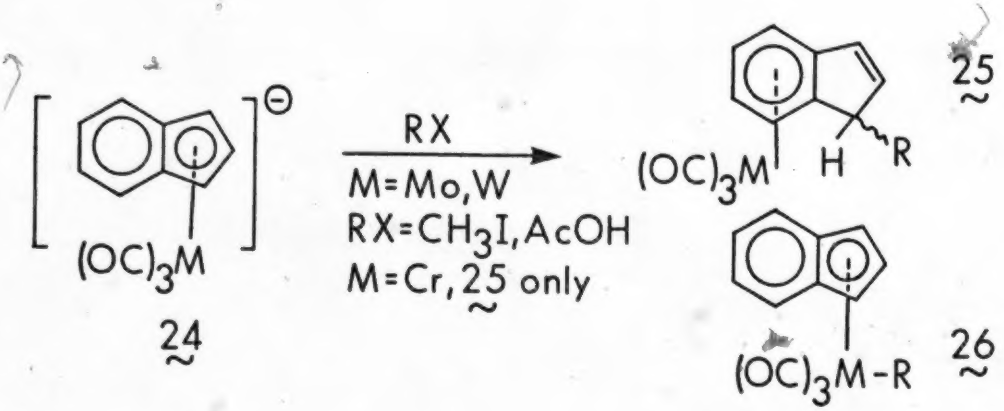
that the cyclopropane ring is stabilized by the depopulation of its highest occupied molecular orbital.[134] Thus when electron withdrawing substituents are present the entire bicyclic structure is stabilized. None of the present substituents fall in this category. Moreover the compound 7-phenyl-7-carbomethoxycycloheptatrienetricarbonyliron, 21d, which contains two electron withdrawing groups on C(7) has a $\Delta G^{\dagger}$-value of 99.9 kJ mol^{-1} [41c] even though the free ligand C_7H_6RR', R = Ph and R' = COOMe, exists as an equilibrium mixture of the cycloheptatriene and norcaradiene forms at ambient temperature in the ratio 1:2.[133] Steric interactions between the C_7-substituents and the cyclohexadiene moiety of the norcaradiene intermediate[137] were given as possible reasons for the unexpectedly high activation energy.[41c] However, some pertinent results were recently communicated in regard to the effect of a π-electron *donor* at C(7) on the cycloheptatriene-norcaradiene equilibrium[135] which could be relevant to the present context. These studies seem to indicate that the replacement of a 7-hydrogen by an electron donating amine group also causes a relative stabilization of the norcaradiene structure. The electronic interactions between the cyclopropyl ring and the π-electron donor are believed to have a total stabilizing influence upon the norcaradiene form. The substituents considered here fall into this category since the strong electron donating ability of the $SiMe_3$ and $GeMe_3$ groups is well-known.[138] Thus it is possible that these substituents could stabilize such an intermediate. Of course, whether such groups do indeed stabilize the norcaradiene intermediate and thereby activate the stepwise 1,2 shifts as the operative mechanism for the fluxional behaviour or promote greater electron delocalization in the cycloheptatriene ring, thereby promoting a "true" 1,3 shift, cannot be determined at the present time. Although the detailed mechanism for the $Fe(CO)_3$ group migration cannot be deduced, it is worth noting that the complexes $\underset{\sim}{21}$ represent rare examples of fluxional molecules rearranging by a net 1,3-shift. Other examples are $(\eta^4\text{-}C_7H_8)Fe(CO)_3$,[41c,d] $(\eta^6\text{-}C_8H_8)Cr(CO)_3$,[42] $Ru_2(CO)_5(C_{16}H_{16})$[40] and cycloheptadienyl and cyclooctadienyl complexes of palladium.[43] We would prefer to close this section by reiterating the experimental observation that small substitutional changes at the C(7) position are apparently sufficient to produce quite visible changes in fluxional behaviour. Or to put it another way, it does not take much to change whimpering into performing dogs in the night-time.[151]

B. Tin and lead derivatives.

a. Synthetic Aspects

As outlined in Scheme IV the compounds 22 (M = Sn, 22a, and Pb, 22b) were obtained from the reaction of the appropriate triphenylmetal chloride with potassium cycloheptatrienyltricarbonylferrate(-1), 16, In contrast to the interaction of 16 with silicon and germanium halides the resulting organometallic compounds contain a metal-metal single bond and an η^3-bound cycloheptatrienyl ring (*vide infra*). The reaction of 16 with $(n\text{-Bu})_3SnCl$ however resulted in the isolation of a mixture of complexes of type 21 and 22 as evidenced by infrared and, particularly, ^{1}H NMR spectra of the isolated material. Subtle effects are apparently controlling the reactivities of these elements since the reaction of 16 with Me_3SnCl also results in both ring and iron substituted products.[41a] For both trialkyltin reagents an approximately 1:1 mixture of the complexes 21 and 22 was obtained.

The formation of the η^3-bound complexes could conceivably result from the direct selective trapping of the η^3-allyl form 16a by the electrophiles. Our inability to induce migration, either thermally or photochemically, of the Ph_3Sn group from the iron center to a ring carbon atom lends some support to the idea that compounds of type 21 and 22 arise from direct initial attack on carbon or iron, respectively. The reactivities of two related anions deserve to be mentioned in this context. The anion $[(\eta\text{-}C_7H_7)Mo(CO)_2]^-$ reacts with Ph_3GeCl and Ph_3SnCl to yield the products $(\eta\text{-}C_7H_7)Mo(CO)_2MPh_3$, M = Ge, Sn.[96b] However, the reaction of $(\eta\text{-}C_7H_7)Mo(CO)_2Cl$ with Me_3CBr in the presence of sodium leads, albeit in very low yields, to $(exo\text{-}7\text{-}C_7H_7CMe_3)Mo(CO)_3$. The particular stereochemistry again indicates addition to a ring carbon atom,[142] even although the reaction is rather complicated as a *tri*carbonylmolybdenum complex results. Ustynyuk and coworkers[145] have communicated their results on the interaction of the $[(indenyl)M(CO)_3]^-$ anion, 24, M = Cr, Mo, and W, with electrophiles, equation (22).



(22)

Depending upon the nature of the group VI metal and upon the particular electrophile, attack seems to occur either at the metal center, product 26, or at the indenyl ligand, product 25.[145] Simultaneous migration of the tricarbonylmetal group to the adjacent ring must also occur in the latter case*.[145] The possibility of interconverting the complexes **25** and **26** has been considered for R = R_3M, M = Si, Ge, Sn,[145] but a detailed account has not been given yet. As the stereochemistry in **25** is not known the site (or sites) of initial attack remain rather obscure for this anion as well.

Using the appearance potentials of the Ph_3Sn^+ ion the iron-tin bond dissociation energy has been calculated as $\sim$249 kJ mol^{-1} in $(C_5H_5)Fe(CO)_2SnPh_3$.[120] Also the transition metal - group IVA metal bond dissociation energies increase on descending group IVA, i.e. D(Fe-Si) < D(Fe-Sn). This is not contradictory to our observation that the reaction of **16** with R_3MCl, M = Si, Ge, leads to ring-substituted compounds (i.e., the formation of a M-C bond) while the interaction of **16** with Ph_3MCl, M = Sn, Pb, produces species containing a Fe-M bond. Moreover, the M-C(sp^3) bond energies decrease (or remain constant) on descending group IVA (Sn-C: $\sim$192 kJ mol^{-1}).[120] In view of these data, our inability to induce Ph_3Sn migration from the iron center to the ring is therefore not surprising. The substantial decrease in D($Fe-SnR_3$) for R = Me relative to R = Ph for the compounds $(C_5H_5)Fe(CO)_2SnMe_3$, D(Fe-Sn) = 222.0 kJ mol^{-1}, and $(C_5H_5)Fe(CO)_2SnPh_3$, D(Fe-Sn) = 249.1

---

*Of course one could postulate the presence of two isomeric forms of anion **24** in solution. Direct attack on the η^6-isomeric form would then result in complex **25**.

kJ mol^{-1},[120] is also reflected in the observation that the reaction of anion 16 with Me_3SnCl results in a mixture of the ring-bonded (21) and metal-tin bonded (22) compounds.

As will be shown later on the complexes reported in this chapter were characterized by mass spectrometry, infrared spectroscopy, elemental analysis and by ^1H and ^{13}C variable temperature nuclear magnetic resonance studies. Although the bonding features of the compounds were clearly indicated, to unequivocally establish the η^3-coordination mode and to have precise structural parameters as guides for the fluxional character (*vide infra*) of these molecules compared to other η^3-C_7H_7 transition metal complexes, it was attempted to determine the molecular structure of the tin derivative by X-ray crystallography.[143] However, it was not possible to refine the structure to an acceptable R-value.[143] Several crystals were considered but to no avail. $(\eta^3\text{-}C_7H_7)Fe(CO)_3SnPhCl_2$, 27, was then characterized crystallographically,[143] in order to be able to relate the structural and fluxional parameters. The complex 27 was obtained from the reaction of 22a with HCl in diethylether.[56] Its structure is shown in Figure XXV, while selected molecular dimensions are given in Table X. The molecular structure of 27, and by analogy, that of 22a, clearly supports the conclusions based upon the spectroscopic characterization of the complexes 22. The synthesis, fluxional behaviour and structure of 27 will not be discussed

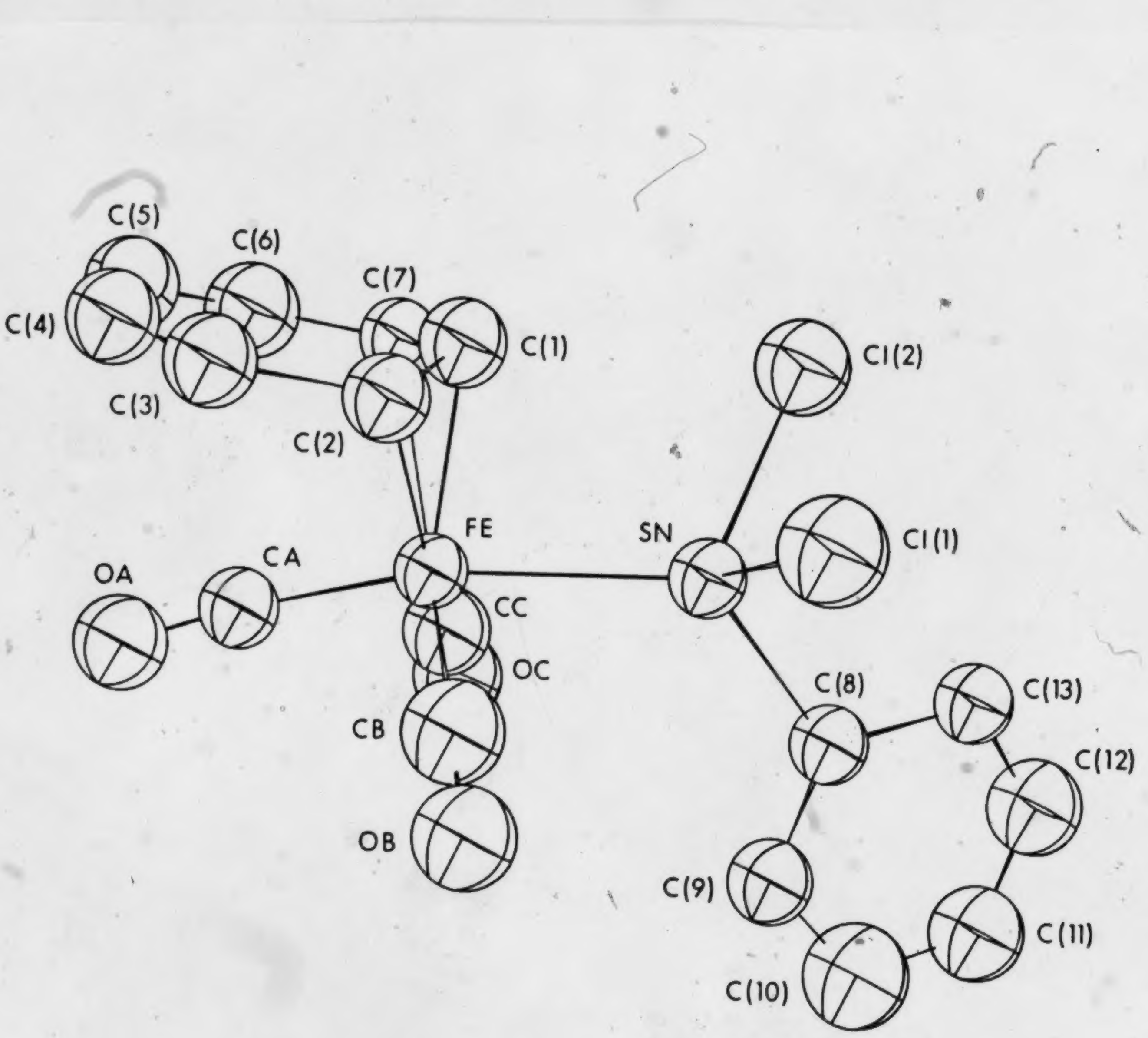

C(5)
C(6)
C(7)
C(4)
C(1)
C(3)
C(2)
Cl(2)
FE
SN
Cl(1)
OA
CA
CC
OC
C(8)
C(13)
CB
C(12)
OB
C(9)
C(11)
C(10)

Figure XXV. Molecular structure of $(\eta^3\text{-}C_7H_7)Fe(CO)_3SnPhCl_2$.[143]

TABLE X

Selected intramolecular distances (Å) and angles (degrees) for the compound $(\eta^3\text{-}C_7H_7)Fe(CO)_3SnPhCl_2$.*

Distances		Angles	
C(1) - C(2)	1.490	CA - Fe - CB	91
C(2) - C(3)	1.495	CA - Fe - CC	86
		CB - Fe - CC	107
		Fe - Sn - Cl(1)	109
C(5) - C(6)	1.304	Fe - Sn - Cl(2)	113
C(6) - C(7)	1.449	Fe - Sn - C(8)	126
		Fe - CA - OA	175
Fe - Sn	2.526	Fe - CB - OB	174
Fe - CA	1.832	Fe - CC - OC	180
Fe - CB	1.785	C(1)-C(2)-C(3)	123
Fe - CC	1.707	C(2)-C(3)-C(4)	136
		C(3)-C(4)-C(5)	126
Fe - C(1)	2.072	C(4)-C(5)-C(6)	124
Fe - C(2)	2.299	C(5)-C(6)-C(7)	131
Fe - C(7)	2.251	C(1)-C(7)-C(6)	128
Sn - Cl(1)	2.387	C(2)-C(1)-C(7)	123
Sn - Cl(2)	2.362		
Sn - C(8)	2.137		

continued...

TABLE X (Continued)

Plane	Atoms	
I	C(1), C(2), and C(7).	Iron is displaced from the plane of these three atoms by 1.886 Å.
II	C(3), C(4), C(5), and C(6).	The four atoms comprising the plane are planar to within 0.03 Å.
III	C(2), C(3), C(6), and C(7).	The four atoms comprising this plane are planar to within 0.04 Å. Atom C(1) is displaced from the plane by 0.30 Å, C(5) by 0.15 Å, and C(4) by 0.10 Å.

Planes	Angles between planes
I + II	146
I + III	154
II + III	173

---

*Preliminary Data.

here as they are outside the scope of the work described in this thesis.[56]

b. Mass Spectral Results

The mass spectroscopic breakdown patterns of the complexes 22 are shown in Table XI. The initial fragmentation of complex 22a typically involves the sequential loss of three carbonyl ligands. Loss of the ligands C_7H_7 and MPh_3 also occurs and ions due to the characteristic breakdown of these groups are observed.[119,120] Important is the observation of peaks corresponding to the ions $FeSnPh_x^+$, x = 3, 2, 1, and 0. The identification of these ions in the mass spectrum of 22a is a clear indication of the presence of a direct iron to tin bond in this complex. It also gives one of the first clues for the change in bonding mode from type 21 to type 22. Noteworthy is the observed base peak at m/e = 224, assigned to the ion $(C_7H_7)FePh^+$. This peak might well arise from the expulsion of a diphenylstannylene group from $(C_7H_7)FeSnPh_3^+$, a metastable peak corresponding to this fragmentation process was observed at m/e = 101.0, in good agreement with the calculated value, m* = 100.8. The reverse reaction, insertion of the sterically demanding stannylene $(Me_3SiCH_2)_2Sn$ into a metal-alkyl bond has been observed.[144]

Spalding has observed highly abundant ions of the type $(C_5H_5)Fe(CO)(L)MR_2^+$ in the mass spectra of the complexes $(C_5H_5)Fe(CO)(L)MR_3$, L = CO, PPh_3, M = Si, Sn, and

D

TABLE XI

Mass spectroscopic data for the complexes

$(\eta^3\text{-}C_7H_7)Fe(CO)_3MPh_3$, M = Sn, Pb.

Assignment	22a[a] m/e	22a[a] rel. abund. (%)	22b[b,e] m/e	22b[b,e] rel. abund. (%)
$C_7H_7Fe(CO)_3MPh_3^+$	582[f]	0.1[c]		
$C_7H_7Fe(CO)_2MPh_3^+$	554[f]	0.5		
$C_7H_7Fe(CO)MPh_3^+$	526[f]	4.1		
$C_7H_7FeMPh_3^+$	498[f]	33.1		
$(C_7H_7FeMPh_2\text{-}H)^+$	420	2.5		
$FeMPh_3^+$	407	0.7		
$(OC)_2FeMPh_2^+$	386	0.2		
MPh_3^+	351	15.6	439	4.3
$C_7H_7FeMPh^+$	344	1.4		
$FeMPh_2^+$	330	12.6		
$(OC)_2FeMPh^+$	309	2.4		
$C_7H_7FePh_2^+$	301	2.0		
$(MPh_2\text{-}H)^+$	273[d]	6.0		
$C_7H_6FeM^+$	266	1.5		
$(FeMPh\text{-}H)^+$	252[d]	9.4		
–	238	2.3		
$C_7H_7FePh^+$	224	100.0	224	28.2
MPh^+	197	42.2	285	1.5
FeM^+	176	6.5	264	0.3

continued...

TABLE XI (Continued)

$C_7H_7Fe^+$	147	36.2	147	28.2
$C_7H_6Fe^+$	146	55.0	146	22.4
M^+	120	12.3	208	1.7
$C_7H_7^+$	91	51.3	91	71.3

[a] T = 130°C; not corrected for ^{13}C. The most abundant ion in each cluster is tabulated, this corresponds for 22a to the ^{120}Sn isotope (relative abundance 32.97%) in the tin containing clusters.

[b] T = 125°C; not corrected for ^{13}C. For each cluster the ion corresponding to the ^{208}Pb isotope (51.7% relative abundance) is reported.

[c] Confirmed by field-desorption mass spectrometry.

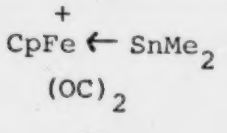
[d] The ions $SnPh_2^+$ and FeSnPh are also observed.

[e] Other intense peaks (rel. abundance) with m/e > 150:

280(5.1), 252(8.6), 182(100.0, $PhC(O)Ph^+$), 167(28.0), 154(64.4, $Ph\text{-}Ph^+$).

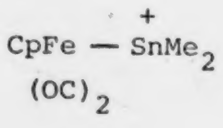
[f] The intensity ratios observed within these clusters agree well with the calculated intensity ratios.

R = Me, Ph or Cl, formed by the loss of a R' radical from the parent ion.[120] An explanation for the stability of these ions was offered by the suggestion that the SnR_2 group might bind to the iron center as a stannylene ligand, 28. Another stable configuration is depicted in 29. In



$$\underset{(\mathrm{OC})_2}{\overset{+}{\mathrm{CpFe}}} \leftarrow \mathrm{SnMe}_2$$

28



$$\underset{(\mathrm{OC})_2}{\mathrm{CpFe}} - \overset{+}{\mathrm{SnMe}_2}$$

29

both cases the iron valence shell contains 18 electrons. We observed similar ions in 22a although with much lower abundances. The complex 22b did not show any ions with m/e-values higher than 439, $PbPh_3^+$, under similar experimental conditions. Ions identified were assigned to: $C_7H_7FePh^+$ at 224, $FePb^+$ at 264, Ph_2CO^+ at 182, Pb^+ at 208, $FeC_7H_7^+$ at 147, $PhCO^+$ at 105 (base peak), and $C_7H_7^+$ at 91. Although this compound evidently is far more labile in the mass spectrometer than its congener, 22b, the ions that are observed indicate that the general features outlined above for 22a are still valid for 22b, i.e. both complexes contain a direct Fe-M bond.

c. Infrared Spectral Data

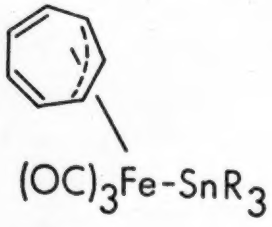
The complexes 22 exhibit three strong well-separated carbonyl stretching frequencies in the 2100-1800 cm^{-1} region, see Table XII. The occurrence of only three bands in the infrared spectrum excludes the possibility of the

TABLE XII

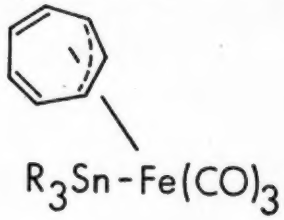
Carbonyl stretching frequencies of the compounds $(\eta^3\text{-}C_7H_7)Fe(CO)_3MPh_3$, M = Sn, Pb in the region 2100-1800 cm^{-1}.

compound	ν_{CO} in cm^{-1}			solvent
22a	2038.5	1987.0	1957.5	n-pentane
22b	2034	1984	1958	hexane

presence of two conformers, 30 and 31, in solution unless



30



31

an accidental overlap of all three bands is occurring. The symmetrical nature of each absorption band seems to negate this argument however. The possible presence of conformational isomers, and their detection by infrared spectroscopy is well-documented in the organometallic literature and has been observed for another η^3-C_7H_7 complex of the transition metals: $(\eta^3$-$C_7H_7)Mo(CO)_2Cp^{63}$ (see Chapter I). As the isomer 30 has been found to represent the solid state structure of 27 it would be reasonable also to assume 30 to be the solution species for both 22a and 22b. The low symmetry found in the crystallographic structure determination of 27, rigorously C_1 and idealized C_s, leads to a prediction of the number of ν_{CO} bands which is concurrent with the experimental observation. The oily and crystalline materials isolated from the reaction of 16 with $(\eta$-$Bu_3)SnCl$ and Me_3SnCl, respectively, show six ν_{CO} frequencies. This is indicative of the presence of geometrical isomers and/or conformers in solution (*vide infra*).

d. ^{1}H NMR Spectroscopic Data

The compounds $(\eta^3\text{-}C_7H_7)Fe(CO)_3MPh_3$, M = Sn, Pb.

Figure XXVI shows the variable temperature ^{1}H NMR spectra of $(C_7H_7)Fe(CO)_3SnPh_3$ in the temperature range 0 to -105°C. The single peak observed for the cycloheptatrienyl hydrogens at ambient temperature establishes unequivocally the fluxional nature of this compound. The chemical shift value of this resonance ($\delta = 5.18$) is indicative of protons attached to an unsubstituted cycloheptatrienyl ring in a non-rigid organometallic compound. This chemical shift value for the dynamic C_7H_7 ligand, at fast exchange, is indeed typical. The single sharp resonances often occur for both η^3, η^5, and η^7 coordination in the region $4.5 \leqslant \delta \leqslant 5.6$ ppm in neutral molecules and at ~6.0 ppm in cationic complexes (*vide infra*). The chemical shift data of the complexes 22 and several related transition metal complexes, which contain the η^3-cycloheptatrienyl ligand, are presented in Table XIII, both limiting and fast exchange spectra are reported. On lowering the temperature the single resonance broadens, collapses, and finally four new resonances in the expected 2:2:2:1 intensity ratio appear. The low temperature limiting spectrum is clearly consistent with the structure found in the solid state. This process is reversible, independent of concentration and independent of solvent (similar spectra were recorded in toluene-d_8, acetone-d_6

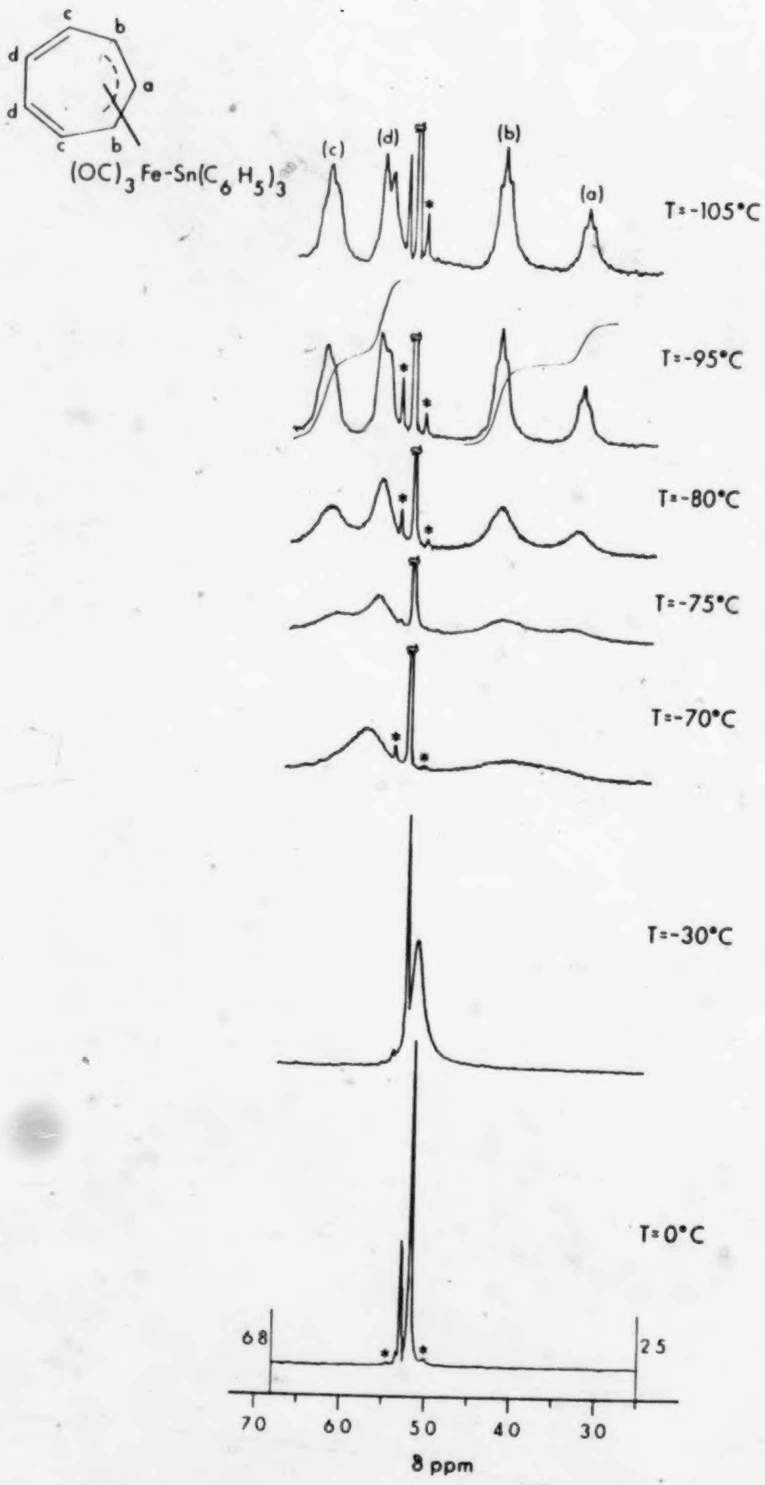


Figure XXVI. Variable temperature ^{1}H NMR spectra of $(C_7H_7)Fe(CO)_3Sn(C_6H_5)_3$ in CD_2Cl_2.

TABLE XIII

^1H and ^{13}C NMR parameters for the compounds $(\eta^3\text{-}C_7H_7)Fe(CO)_3MPh_3$, M = Sn, Pb and for related complexes containing an η^3-bound C_7H_7 moiety.[a]

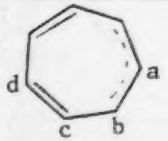
Compound	Solvent	Assignment a	 b	 c	 d	Temp (°C)	$\delta(C_7H_7)$ at fast exchange limit Obs	 Calc	Ref.
^1H Data									
22a	CD_2Cl_2	3.36	4.36	6.40	5.71	-105	5.18	5.19	This work
	toluene-d_8	3.40	4.35	5.80 - 5.65		-100	5.13	5.00[b]	This work
22b	CD_2Cl_2	3.46	4.59	6.32	5.68	-100	5.25	5.23	This work
8	$CHFCl_2$	2.32	4.59	6.50	5.40	-118	4.98	5.04	63a
	Cl_2F_2/toluene-d_8(1/1)	1.20	3.84	6.47	5.46	-102	4.69	4.68	63a
	$CFCl_3/CS_2$(1/2)	2.10	4.27	6.0	5.00	-110	-[d]	4.66	64
11[h]	$CDCl_3$	4.98	4.50	3.83	5.40	-71	4.57	4.63	64
	$CDCl_3$/toluene-d_8(4/1)	4.82	4.37	3.77	5.37	-71	-[d]	4.55	64
3	CF_2Cl_2	3.5	4.95	~6.5	~5.8	-140	-[d]	5.43	60
9	toluene-d_8	2.44	4.32	6.05	5.20	-50	4.8	4.80	61
	$CDCl_3$	3.08	4.75	6.10	5.15	-18	-[d]	5.01	61

continued...

TABLE XIII (Continued)

10[e]	CD_2Cl_2	1.15	5.26	6.96	5.75	<-42[c]	-[d]	5.30	62
11[e]	CD_2Cl_2	4.59	5.13	3.98	5.52	-42	4.80[f]	4.84	62
^{13}C Data									
22a	CD_2Cl_2	58.7	67.5	122.2[g]	g	-85	102.7	-	This work
22b	CD_2Cl_2	60.7	68.4	122.2[g]	g	-95	102.8	-	This work
32	CD_2Cl_2/CS_2	51.0	64.6	121.0	137.2	-117	100.6	99.5	139

[a] In δ ppm.



[b] See text.

[c] The temperature at which the limiting spectrum was recorded has not been reported.

[d] The chemical shift value of the C_7H_7 ligand at fast exchange has not been reported.

[e] $L = HBpz_3$.

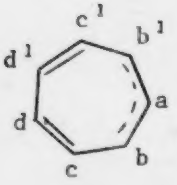
[f] This resonance at δ = 4.80 was 0.58 ppm wide at half height at 25°C in dichloromethane-d_2; in toluene at 83° a sharp peak with $w_{1/2}$ = 0.02 ppm is observed at δ = 4.50.

[g] The resonances due to one set of the diene carbon atoms fall amidst the phenyl carbon resonances. The indicated assignment is discussed in the text.

[h] $L = (C_5H_5)$.

and $CFHCl_2/CD_2Cl_2$ (4/1) solvent mixtures). The coalescence temperature of the four individual resonances is ~-60°C.

An unambiguous assignment of the resonances observed in the low temperature limiting spectrum is of utmost importance if one is to determine the governing exchange mechanism. With the assignment of the resonance of intensity 1 at δ 3.36 ppm to the central allylic proton a and aided by homonuclear experiments, all resonances can be assigned. Thus irradiation of proton a resulted in the collapse of the triplet-like structure of the resonance at δ 4.36 into a doublet. Similarly irradiation of this resonance, assigned to the outer allylic protons b, resulted in a significant change in the appearance of the resonance at δ 6.40 (protons c) but did not affect the signal at δ 5.71 (protons d). Decoupling of the latter two resonances further supported the above assignment. The unique assignment thus obtained and the deduced coupling constants are shown below and in Table XIII. As can be seen from the table the proposed assignments are in agreement with previous



a	b	c	d
3.36(1H,t)	4.36(2H,m)	6.40(2H,m)	5.71(2H,dd)

J_{ab} = 5.9 Hz, J_{bc} = 6.9 Hz, J_{cd} = 10.0 Hz, $J_{cd'}$ = $J_{c'd}$ = 2.4 Hz (all ± 0.3 Hz).

results and confirm that: (i) the protons c, the "outer-diene" protons, resonate at lower field than the "inner-diene" hydrogens d. As seen in Table XIII this is generally the case in η^3-cycloheptatrienyl complexes, although unambiguous assignments could not always be obtained. (ii) The resonance due to the outer allylic protons is at considerably lower field than the resonance due to the central proton a. This is indicative of a η^3-cycloheptatrienyl ligand* and contrast remarkably the situation in η^3-allyl complexes.[140] The large change in the chemical shift value of the outer-diene protons on changing the solvent from dichloromethane to toluene is to be noted. Similar shifts are observed for the protons a and b in the complex $(C_7H_7)Mo(CO)_2Cp$.[63a]

The reaction of $[(C_7H_7)Fe(CO)_3]^-$ with tri(alkyl)tin chlorides. ^1H NMR spectroscopic data.

The reaction of 16 with $(n\text{-}Bu)_3SnCl$ has been mentioned. Both trialkyltin halide species, Me_3SnCl[152] and $(n\text{-}Bu)_3SnCl$ react with the anion 16 to yield mixtures of the compounds 21 and 22. Here we like to discuss the evidence leading to the conclusion that both isomers are present.

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*In complexes containing a η^5-C_7H_7 ligand the single central proton resonates at much lower field and generally carries the lowest δ value observed for any of the ring protons in the ^1H NMR spectrum of a static η^5-C_7H_7 ligand (see Chapter VI).

The ^{1}H NMR spectrum of the crystalline solid obtained in the reaction of Me_3SnCl with **16**[152] is shown in Figure XXVII while the variable temperature spectra are presented in Figure XXVIII. Similar spectra were obtained for R = n-Bu. The presence of two singlets in the methyl region together with the six carbonyl stretching bands in the infrared spectrum clearly indicates the presence of two isomers or conformers. Moreover there is one sharp singlet at δ 5.00 ppm, in toluene-d_8, which broadens and collapses into the baseline upon lowering the temperature. This behaviour is typical for a species of type **22**. The resonances of the cycloheptatrienyl protons of the ring-substituted isomer are also observable even though, at ambient temperature, their individual intensity is rather low compared to the collective intensity of the cycloheptatrienyl protons of **22c** ($R_3M = Me_3Sn$). Upon the collapse of the latter singlet at temperatures below -30°C these resonances clearly become more distinct although somewhat different in appearance from the spectra of **22a** and **22b**. It follows from the integration ratio of the Me_3Sn singlets that the two compounds are present in the approximate ratio 3:2, **22c** being the more abundant species. Completely analogous observations have been made for the tri(n-butyl)-tin derivatives. In this case the sharp singlet for the protons of the cycloheptatrienyl group in **22d** (R_3M = $(n\text{-}Bu)_3Sn$) appears at δ 5.20 ppm (in dichloromethane-d_2).

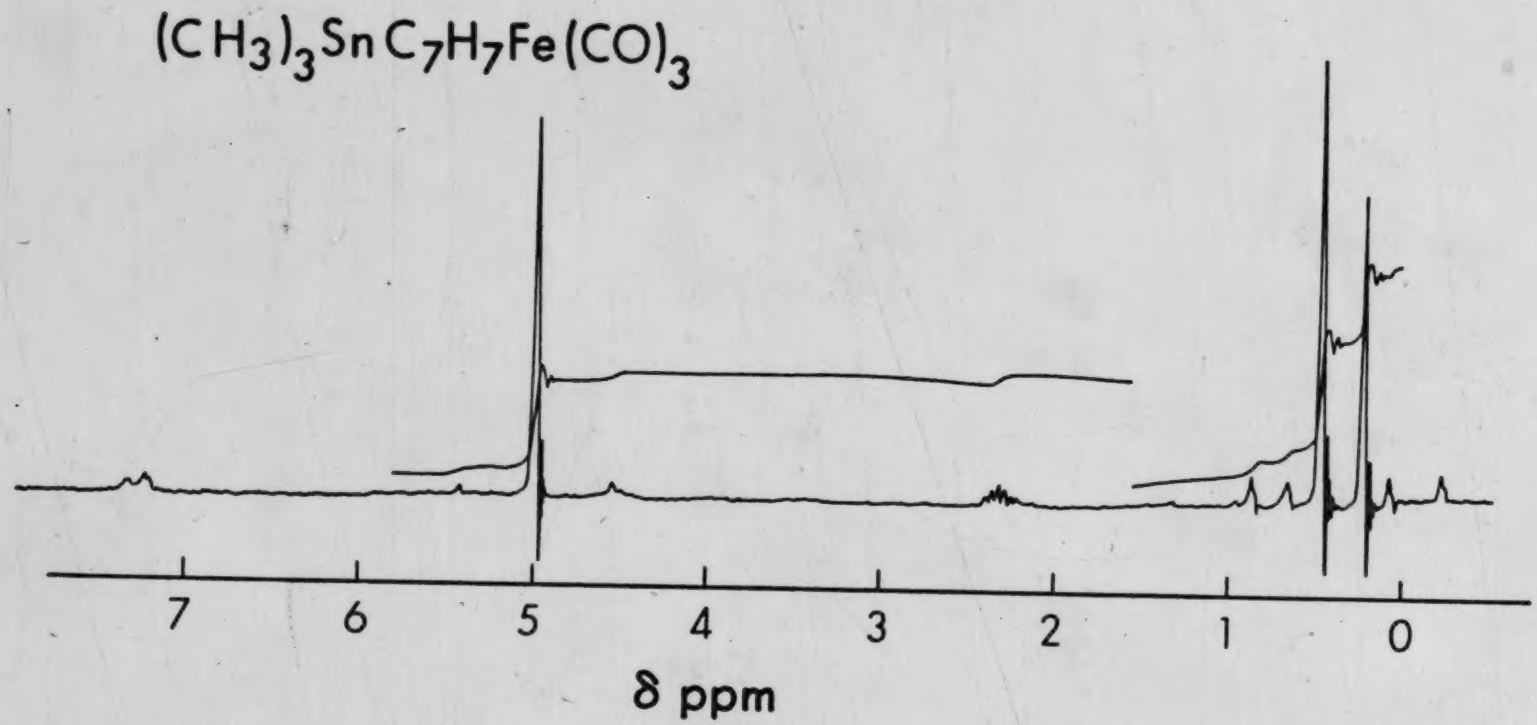


Figure XXVII. ^1H NMR spectrum of the mixture of the isomeric complexes (η^4-$C_7H_7SnMe_3$)$Fe(CO)_3$ and (η^3-C_7H_7)$Fe(CO)_3SnMe_3$.

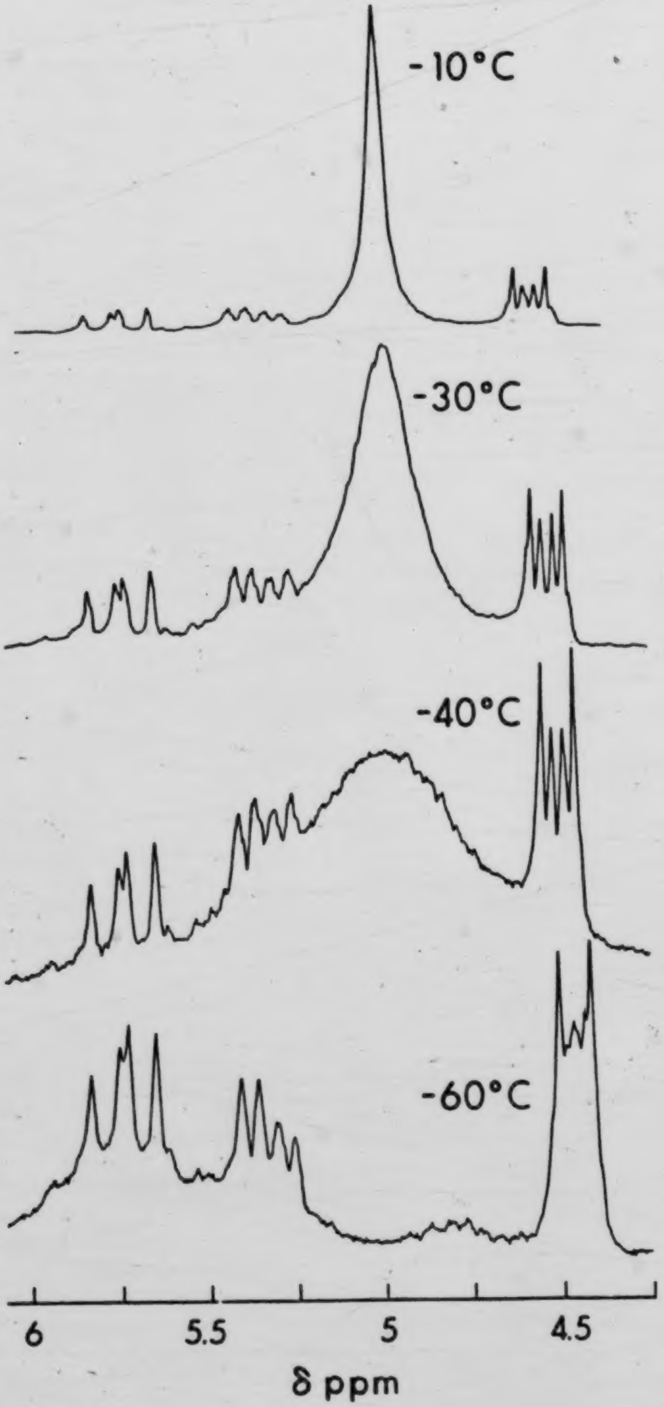


Figure XXVIII. Variable temperature ^1H NMR of the mixture of the iosmeric complexes (η^4-C_7H_7-$SnMe_3$)Fe(CO)$_3$ and (η^3-C_7H_7)Fe(CO)$_3$$SnMe_3$.

The variable temperature profile of the trialkyltin derivatives, 22c and 22d, is similar and resembles that of the triphenyltin derivative 22a. The complicated nature of the n-Bu region prevented the calculation of the isomer ratio from the ^{1}H NMR spectrum but from the infrared spectra it was concluded that the two geometrical isomers are present in approximately a 1:1 ratio. Finally it is noted that the existence of an equilibrium between the two isomeric forms in addition to the fluxional behaviour of the η^3-bound cycloheptatrienyl isomer cannot be ruled out for these trialkyltin derivatives.

e. Fluxional Processes

Mechanism of the rearrangement involving the seven-membered ring.

With an unambiguous assignment of the ring resonances at our disposal we are able to elucidate the predominant pathway for rearrangement. From Figure XXVI it is evident that the resonance which is now assigned to the inner diene protons d of the seven-membered ring collapses at a much slower rate than the other three remaining resonances. Particularly the allyl resonances broaden with a very similar rate.

The slower line broadening of the inner-diene proton resonances compared to the other signals immediately rules out the random shift of the $Fe(CO)_3SnPh_3$ fragment as a plausible mechanism since this would demand a symmetrical coalescence of all resonances. A delineation between the remaining distinct 1,2-, 1,3-, and 1,4-$Fe(CO)_3SnPh_3$ shifts can be made by a careful examination of the interchanges of the proton environments produced upon executing each of these shifts. This can be seen in Scheme I (Chapter I). It is clear from this Scheme that the 1,2 shift leaves the environment of one of the inner-diene protons unchanged whereas the 1,3 shift leaves one of the outer allylic protons in an identical position, while the 1,4 shift does not change the environment of one of the outer-diene protons. Since the resonances from which the nuclei leave faster will also broaden faster, the above results would lead to the expectation of a sharper d-resonance during the initial stages of line broadening in the case of a 1,2 shift only. It is evident that the experimental observations are thus compatible with a 1,2 shift of the $Fe(CO)_3SnPh_3$ moiety as the major rearrangement process in these complexes. The similar line broadening observed for the analogous lead complex mitigates for a 1,2 migration in this compound also. These results are not surprising since it is well recognized[22b,24] that the 1,2 shift is the dominant mode of metal migration in "ring-whizzers."

Activation parameters for the 1,2-shift of the $Fe(CO)_3SnPh_3$ moiety.

The ^1H NMR spectra of 22a in the temperature range -70 to -105°C were simulated by use of the computer program DNMR4.[147] Not only could the 1,2-shift be confirmed as the major pathway for the rearrangement by comparing the calculated spectra for the 1,2-, 1,3-, and 1,4- shift with the experimental spectra but an approximate value of $\Delta G^{\ddagger}$ could be extracted as well by fitting the calculated spectra to the observed spectra. At several temperatures an estimate of the specific rate constants for the rearrangement process could thus be obtained and this is shown in Figure XXIX. No explicit account was taken of spin-spin coupling. Instead, the T_2 relaxation times of the exchanging sites in the absence of exchange were set equal and adjusted to give linewidths at slow exchange which approximate to those in the observed spectra.[148,24,33a] The linewidth at half height, $w_{1/2}$, is related to T_2 in the abscence of exchange by $T_2^{-1} = \pi(w_{1/2})$. In general the effect of coupling upon the exchange rate cannot be readily estimated.[24] Nevertheless, the exchange rate for coalescence is considered to be rather insensitive to the presence of coupling particularly when the chemical shift differences are much larger than the coupling constants.[24,33b] After the rate constants had been obtained a plot of ln(rate/T) versus 1/T yielded the activation

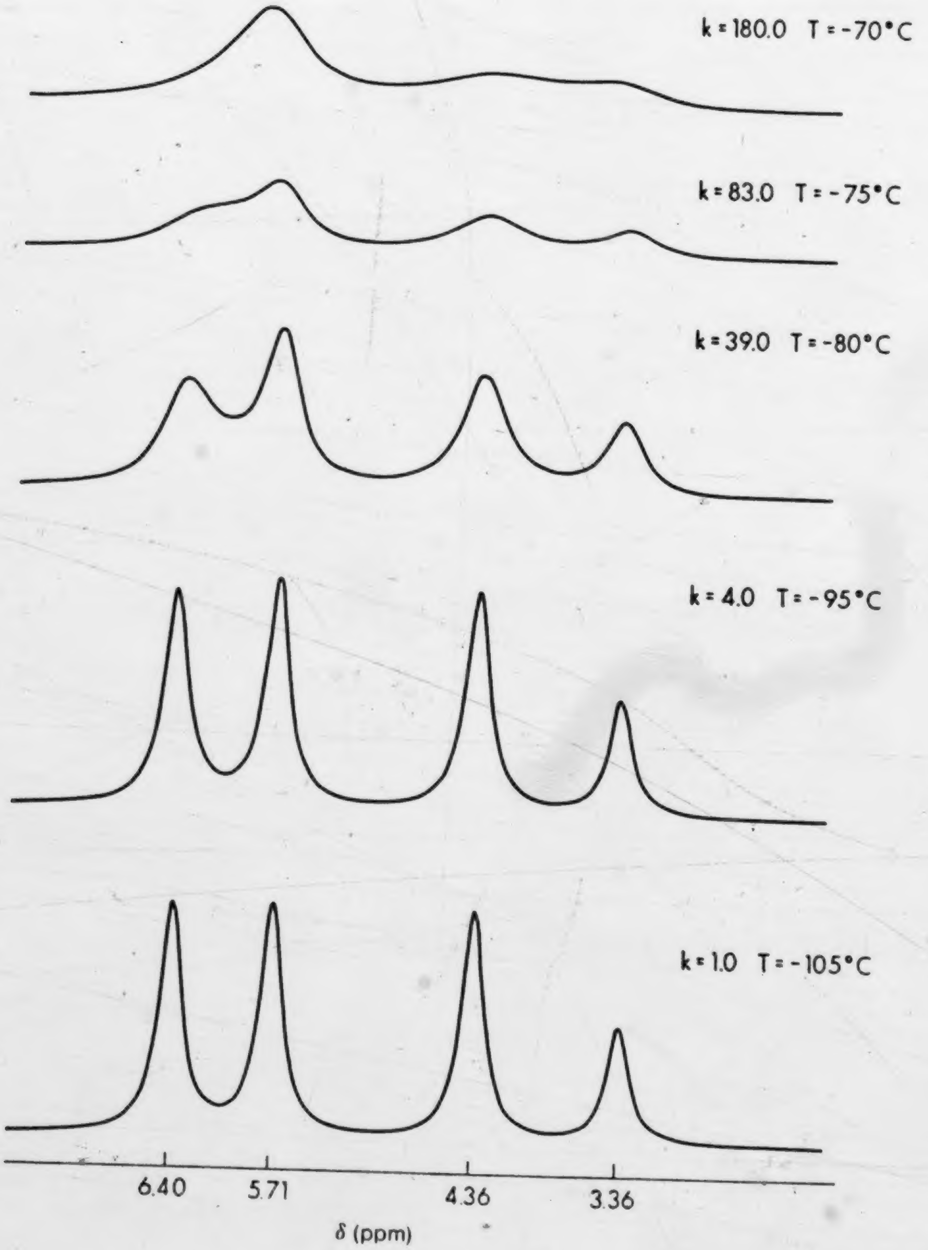


Figure XXIX. Calculated ^{1}H NMR spectra of $(\eta^3\text{-}C_7H_7)Fe(CO)_3\text{-}Sn(C_6H_5)_3$ for several mean residence times (assuming a 1,2 shift mechanism; T_2 = 0.019).

parameters: $\Delta H^{\ddagger} = 40.5$ kJ mol^{-1}, $\Delta S^{\ddagger} = 0.2$ Jk^{-1} mol^{-1}, and $\Delta G^{\ddagger}_{273} = 40.5$ kJ mol^{-1}. The chemical shift values and the temperature profile of the proton resonances for the complex 22b are very similar to those of 22a. A slightly lower T_c indicates that the 1,2-shift process is more facile for 22b however. Within the error limits (estimated to the ~6 kJ mol^{-1}) the two $\Delta G^{\ddagger}$-values for the compounds 22 are nevertheless considered to be equal.

f. ^{13}C NMR spectroscopic data.

The C_7H_7 ligand.

The variable temperature ^{13}C NMR spectra of the complexes 22a and 22b are shown in Figure XXX and XXXI, respectively, and the chemical shift data are summarized in Table XIII. At ambient temperature a single resonance is observed for the ring carbon atoms, as the temperature is lowered the resonance collapses and disappears into the baseline. In both cases separate signals can be seen for three of the four different carbon atoms below -80°C. Unfortunately, the fourth resonance is hidden among the resonances of the phenyl carbon atoms. Due to our inability to observe this remaining resonance no definite assignment of the diene resonances could be made. The allylic signals could be assigned by double irradiation experiments (Table XIII). Recently the ^{13}C NMR spectrum of a related complex, (η^3-cycloheptatrienyl)(η^5-diphenylmethylcyclopentadienyl)-dicarbonylchromium (32), has been reported.[139] Significantly

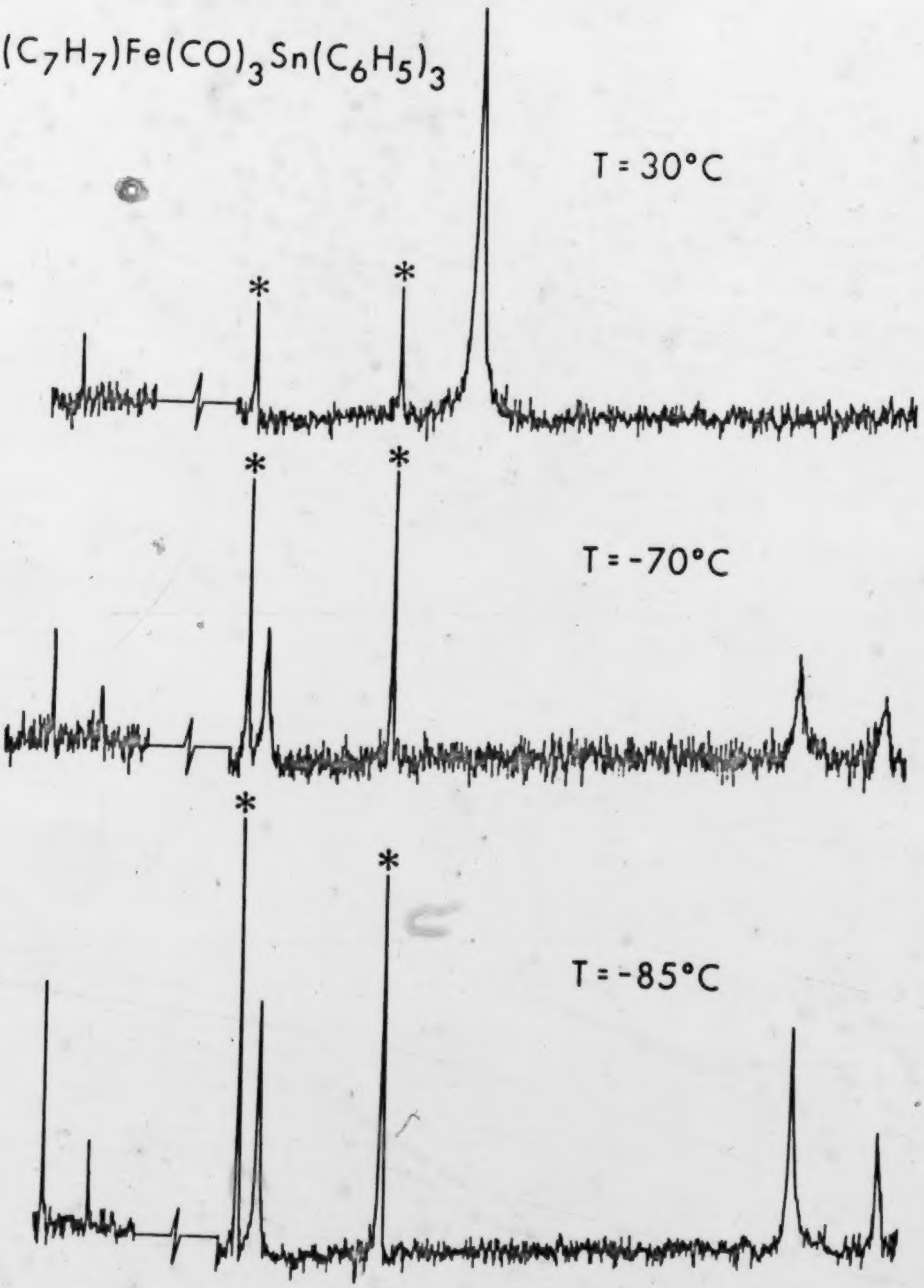


Figure XXX. ^{13}C NMR $(C_7H_7)Fe(CO)_3Sn(C_6H_5)_3$ in $CD_2Cl_2/CHFCl_2$ (3/1).

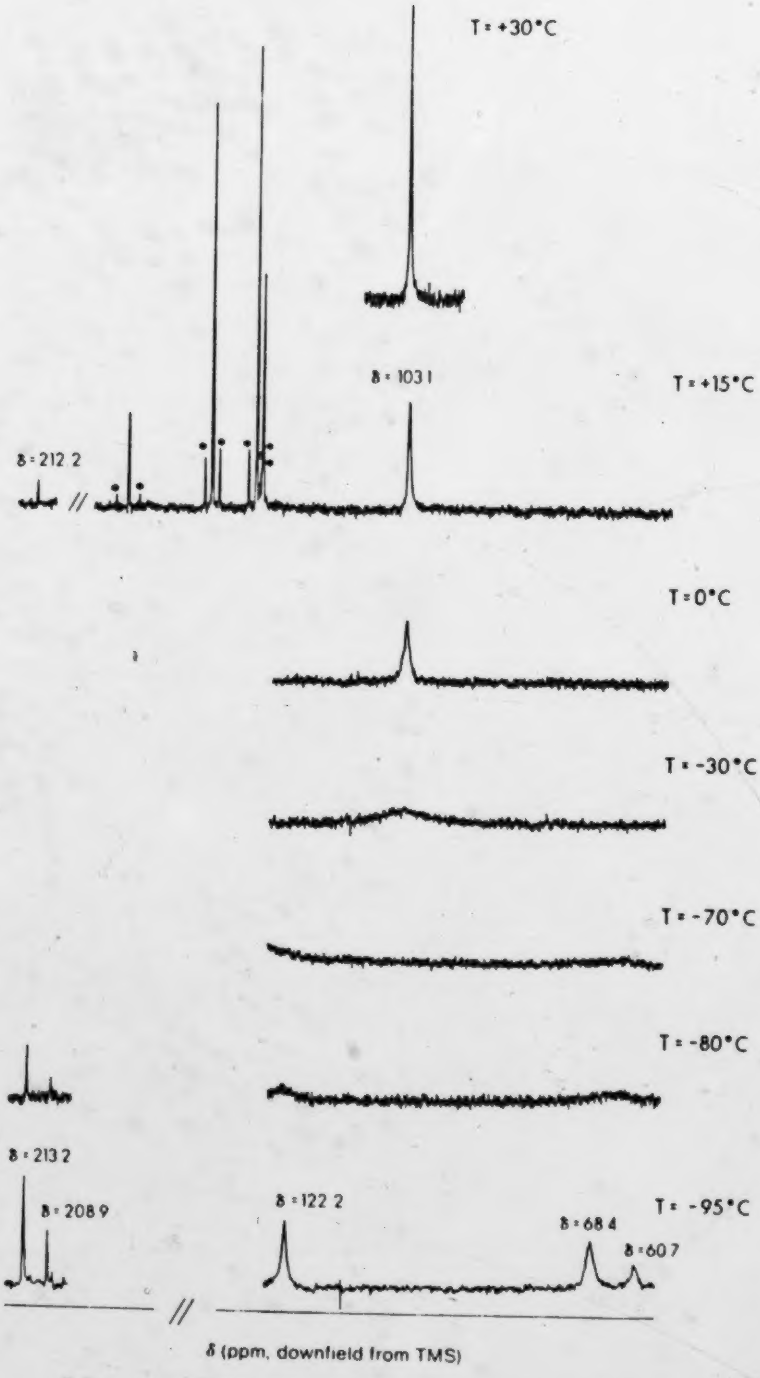


Figure XXXI. ^{13}C Variable Temperature NMR Spectra of $(\eta^3\text{-}C_7H_7)Fe(CO)_3Pb(C_6H_5)_3$ in CD_2Cl_2. (*-207 Pb satellites).

the ^{13}C chemical shift values of the cycloheptatrienyl ring in 32, agree well with those reported here, and on this basis a tentative assignment for the c and d carbon resonances would be possible. In the absence of supporting evidence this assignment is ambiguous however. A value of δ140.5 ppm can be calculated for the chemical shift value of the hidden resonance from the high temperature averaged chemical shift value of the cycloheptatrienyl carbons in 22a and the δ-values of the three resonances distinguishable at -85°C. This value fits the pattern set by the ^{13}C resonances of 32 (Table XIII). A careful examination of the variable temperature profiles shows that the two allyl resonances, both in 22a and in 22b, collapse at the same rate therewith ruling out the 1,3-shift as an important rearrangement pathway. It is unfortunate that one set of carbon atoms is hidden by the phenyl resonances since information about the free energy of activation for the migration of the $Fe(CO)_3SnPh_3$ fragment around the C_7H_7 ring is thus not available from the carbon-13 NMR data, whereas the value from the ^1H NMR data is subjected to uncertainties due to the neglect of the coupling constants.

Carbonyl ligands.

The scrambling of the carbonyl ligands in the complexes 22 is most clearly seen in Figures XXX and XXXI. The single sharp signal at ambient temperature represents all three carbonyl ligands while below -70°C separate resonances for the carbonyl ligands become visible. The presence of two signals in the intensity ratio 2:1 also shows the effective C_s-symmetry of the molecule, again being consistent with the structural information. In order to compare the energetics of the carbonyl scrambling and 1,2-shift processes we determined the $\Delta G^{\ddagger}$-values for the former process. The most accurate procedure to obtain these activation parameters is by fitting calculated spectra to the observed spectra and thus extracting the rate constants at several different temperatures. A plot of ln(k/T) versus 1/T, and a subsequent least-square analysis to find the slope and intercept of the best-fit straight line through the data points, will lead to the desired parameters. To circumvent this tedious, time-consuming, and expensive procedure several short-cuts have been used.[149,150] The simple formula for a two-site equal-population exchange problem can be used, equation (6).[149]

Bar-Eli[150] and co-workers determined the values of $\Delta G^{\ddagger}$ for a two-site unequal population problem by the use of equation (23), where ΔP is the difference in population

$$\Delta G^{\ddagger}_{T_c} = 19.13\ T_c\ (10.62 + \log\ \{\frac{X}{2\pi(1 \pm \Delta P)}\} + \log\ \{\frac{T_c}{\Delta\nu}\})\ (23)$$

of the two sites under no exchange conditions (0.334 in the present case), $X = 2\pi(\Delta\nu)\tau$, and τ is the lifetime.

The value of log $(X/(2\pi(1 \pm \Delta P))$ can be evaluated from a graph in the paper which gives the values of this term as a function of ΔP.

In order to compare the results of these three methods, e.g. line shape analysis and the formulae for equal and different populations, we have calculated $\Delta G^{\ddagger}_{T_c}$ by each of these procedures; the results are shown in Table XIV together with the δ_{CO} ^{13}C-chemical shift data.

The scrambling of carbonyl ligands within tricarbonylmetal moieties has been reviewed recently by Cotton.[91] A summary of the E_a and $\Delta G^{\ddagger}$ values observed for these processes has also been given and values of 35-50 kJ mol^{-1} for the free energy of activation are common.[91] The $\Delta G^{\ddagger}$-values obtained for 22a and 22b fall into this range. A reasonable agreement between the three methods for calculating $\Delta G^{\ddagger}$ is observed with the value obtained by line shape analysis being slightly higher in 22b. Although the activation parameters for both "ring-whizzing" and carbonyl scrambling are rather similar, because of the uncertainties associated with the ^{1}H NMR data and the relatively poor quality of the carbonyl data it is impossible to determine with certainty whether the two processes are coupled together and proceed by the same mechanism.

TABLE XIV

^{13}C NMR data in the carbonyl region for the complexes $(C_7H_7)Fe(CO)_3MPh_3$ and a comparison of the $\Delta G^{\ddagger}$-values for carbonyl scrambling as obtained by different methods (M = Sn, Pb).[a,b]

Compound	Chemical Shift (2)	(1)	T_c (°C)	$\Delta\nu$ (Hz)	$\Delta G^{\ddagger}$ (at T_c) (kJ mol^{-1}) 1	2	3
22a	213.6	208.6	-50	113	43.8	43.9	–[c]
22b	213.2	208.9	-70	97	40.0	40.1	45.8

[a] In δ (ppm) at -85°C (M = Sn) or -95° (M = Pb).

[b] 1, two-site equal population formula.
2, two-site unequal population formula.
3, line shape analysis.
For the methods 1 and 2 $\Delta G^{\ddagger}$ is given for the exchange rate k_{12}, i.e., from the site of population 0.33 to the site of population 0.67.

[c] No reliable value could be obtained due to poor resolution at $T \cong T_c$.

g. Relationships between the structural and fluxional parameters of η^3-cycloheptatrienyl complexes of the transition metals.

Due to the accidental overlap of one of the resonances of the seven-membered ring with the phenyl carbon atom signals in the compounds 22 no additional information regarding the 1,2-shift could be obtained although the ^{13}C NMR spectra support the conclusions based upon the ^1H NMR data. However, it is evident that, in general, the larger chemical shift differences and the absence of coupling between the resonances in the carbon-13 spectra will create a more convenient route towards the elucidation of the rearrangement processes and the determination of the activation parameters than the proton NMR spectra. Although ^{13}C NMR studies have been elegantly applied to other fluxional molecules,[25] the present data form, together with the recently reported data for 32,[139] the first characterization of η^3-C_7H_7 transition metal complexes by ^{13}C NMR spectroscopy. The activation parameters for the 1,2 $Fe(CO)_3SnPh_3$ shifts are subjected to uncertainties but it is nevertheless considered instructive to compare the free energies of activation of related organometallic complexes containing an η^3-bound cycloheptatrienyl ligand with the present data in view of the structural and fluxional data available. The available data are reviewed in Table XV.

TABLE XV

Structural and fluxional characteristics of some η^3-cycloheptatrienyl complexes of the transition metals.

Compound		T_c (°C)	$\Delta G^{\ddagger}_{T_c}$ (kJ mol^{-1})	α (deg.)	C(2)-C(3) (Å)	Ref.
$(C_7H_7)Fe(CO)_3SnPh_3$	**22a**	-60	40.5	–	–	This work
$(C_7H_7)Fe(CO)_3PbPh_3$	**22b**	-65	~40	–	–	This work
$(C_7H_7)Fe(CO)_3SnPhCl_2$	**27**	-100	–	–	1.490	56,143
$(C_7H_7)Mo(CO)_2(C_5H_5)$	**8**	~-60	(~38.9)[a]	14.7	1.45	64
$(C_7H_7)Mo(CO)_2L^b$	**10**	~-60	–	b	b	62
$(OC)_3Fe(C_7H_7)Rh(CO)_2$	**33**	<-164	<25	22.8	1.45	112
$(OC)_3Fe(C_7H_7)Mo(CO)_2$-(C_5H_5)	**11**	-3	52±5[c]	61.0	1.50	64
$[(C_7H_7)Fe(CO)_3]^-$	**16**	<-140	<25	15.1[d]	1.425	This work, 107

FOOTNOTES FOR TABLE XV

[a] Difficulties have been encountered in determining the activation parameters for this compound, $36.8 \leqslant \Delta G^{\ddagger} \leqslant 40.5$ and $E_a = 52 \pm 3$ kJ mol^{-1} with log $A = 16.0 \pm 0.6$. See footnote 16 in reference 63a.

[b] $L = H_2B(3,5\text{-pz})_2$. Although the X-ray structure determination of this compound has been reported,[62a] no information regarding the values of α or C(2)-C(3) is available. In a related compound, with $L = pz_3BPh$, C(2)-C(3) = 1.457.[62d]

[c] $E_a = 54 \pm 4$ has been reported;[64] $\Delta H^{\ddagger} = E_a - RT$, and the value of $T\Delta S^{\ddagger}$ has been assumed to be zero for the above calculation of $\Delta G^{\ddagger}$.

[d] Personal communication from H. Behrens (α was determined as 14.5° and 15.7° respectively, from which the averaged value of 15.1° is obtained), February 1979 (University of Erlangen, West-Germany).

Particularly we consider the angle α, defined as the angle between the π-orbitals of the outer carbon atoms of the two sets of bonding fragments, the allyl and diene moieties, in the cycloheptatrienyl ring. Each π-orbital is assumed to be perpendicular to the plane of the carbon atom involved, C(2) or C(3), and its neighboring atoms.[64a,112] Increasing overlap and therewith increasing fluxionality would then be indicated by a smaller value of the angle α and a shorter C(2)-C(3) distance, if no other factors are important. It is immediately clear from the limited examples in Table XV that the coordination of a second transition metal to the cycloheptatrienyl ring has a marked effect upon the fluxionality. If the two metals are coordinated to the ring in a cis-arrangement as in $(OC)_3Fe(C_7H_7)Rh(CO)_2$, 33a,[112] the angle α is small, 22.8°, and an extremely fluxional molecule is observed. However, if a trans-arrangement of the two metals to the ring occurs the angle α opens, the distance C(2)-C(3) becomes longer and the coalescence temperature increases upon the coordination of the second transition metal moiety to the ring. This is observed most clearly by comparing the compounds $(C_7H_7)Mo(CO)_2Cp$ and trans-$(OC)_3Fe(C_7H_7)Mo(CO)_2Cp$, but similar observations have been made for the complexes $(C_8H_8)Fe(CO)_3$ and trans-$(OC)_3Fe(C_8H_8)Fe(CO)_3$ [9,64] and $(C_7H_7)Mo(CO)_3L$ and $(OC)_3Fe(C_7H_7)Mo(CO)_3L$,[62c] in which L represents a variety of polypyrazolylborate ligands.

A correlation for the mononuclear components is less obvious. The small value of α and the short C(2)-C(3) distance found for anion **16** [107] account nicely for its high fluxionality. The neutral complexes, **8**, **22**, and **27** do not reveal a distinct trend. The small value of α (14.7) in **8** is disturbing in view of the rather high coalescence temperature (~-60°C) for this compound, particularly if contrasted to the values of α and T_c in anion **16**. We also note that the stepwise substitution of Cl for Ph in **22a** (leading to derivatives of the type $-SnPh_2Cl$, $-SnPhCl_2$ (**27**), and $-SnCl_3$ [56]) appears to lower the coalescence temperature.[56] A general qualitative relation is difficult to discern and this is aggravated by a lack of structural data for most of the mononuclear η^3-cycloheptatrienyl complexes. It appears that other factors, such as the effective charge of the fluxional species, could be important as well in determining the extent of fluxionality in these complexes. Steric considerations also should not be neglected. In **27**, for example, the cycloheptatrienyl ring is clearly pointing away from the $SnPhCl_2$ substituent and, if this is the result of intramolecular non-bonding interactions, similar steric effects will play an even more important role in the compounds **22**. To better understand any relation that might exist between the structural and fluxional parameters of these compounds, additional information regarding the molecular structures of η^3-C_7H_7 complexes of the transition metals is required.

Conclusions

η^4-cycloheptatrienetricarbonyliron can be deprotonated in a variety of ways to give the anion $[(C_7H_7)Fe(CO)_3]^-$. The reaction of this anion with main group IV electrophiles results in the formation of two structurally different types of complexes which show an interesting stereochemically nonrigid behaviour on the NMR time scale.

The metathesis reaction of 16 with the silicon and germanium electrophiles R_3MCl, R = Me, M = Si or Ge, and R = Ph, M = Ge results in the facile synthesis of substituted η^4-bound cycloheptatrienetricarbonyliron species. In contrast 16 reacts with triphenyltin chloride and with triphenyllead chloride to yield the compounds $(\eta^3-C_7H_7)-Fe(CO)_3MPh_3$, M = Sn and Pb in good yield. The cycloheptatrienyl ring in the latter complexes is bound in an η^3- fashion while the compounds also contain a single metal-metal bond. No reaction is observed between $[(C_7H_7)Fe(CO)_3]^-$ and Ph_3SiCl and Me_3SiCH_2Cl from which the moderate nucleophilicity of the anion can be deduced. With these results we have been able to arrive at a discrimination in the reactivity of 16 towards group IV electrophiles. Although we do not imply the selective trapping of the two postulated isomeric forms of $[(C_7H_7)-Fe(CO)_3]^-$, 16a and 16b, in these reactions, the final reaction products are clearly dependent upon the nature of the main group element: Ph_3SiCl does not react with

16, Ph_3GeBr yields the ring-substituted species $(\eta^4-C_7H_7GePh_3)Fe(CO)_3$, and Ph_3SnCl and Ph_3PbCl produce the compounds $(\eta^3-C_7H_7)Fe(CO)_3MPh_3$. The main objective of this particular project has therewith been realized.

The stereochemically nonrigid character of the compounds **21** and **22** has been studied by means of variable temperature ^1H and ^{13}C NMR spectroscopic studies. At elevated temperatures a nonrigid behaviour of the complexes **21** becomes detectible, which results in the pair-wise averaging of the olefinic hydrogen and carbon atom resonances while the signals due to H(7) and C(7) remain unaffected by the rearrangement process. A 1,3-shift of the $Fe(CO)_3$ moiety nicely accounts for the observed spectral changes. A direct 1,3-shift or two consecutive 1,2-shifts, with a substituted norcaradiene species as an intermediate, are both compatible with the observed data and are regarded as the most plausible mechanisms. The free energies of activation for this rearrangement process in the complexes **21** are in the order of 65-75 kJ mol^{-1}, a substantial decrease from the value for the unsubstituted parent molecule. Of course the synthesis and study of a larger number of substituted cycloheptatriene complexes of type **21** by, for example, the spin saturation transfer technique would enhance our understanding of the precise nature of the physical pathway for rearrangement. The effects of both electron withdrawing, electron releasing, and sterically demanding substituents on the energetics of the rearrangement deserve a thorough scrutiny in order for the authentic operative shift to be revealed.

The fluxional behaviour of the complexes **22** is best described by a dominant 1,2-shift of the $Fe(CO)_3SnPh_3$ moiety with respect to the η^3-bound cycloheptatrienyl ring. Most important to the delineation of this shift as the operative mechanism was our ability to assign *each* resonance in the low temperature ^1H NMR spectrum. The free energy of activation for this process is 35-45 kJ mol^{-1} which is similar to the value of the $\Delta G^\ddagger$ found for the scrambling of the carbonyl ligands. The reactivity of both types of compounds, **21** and **22**, is being pursued. In particular the complexes **22** are potentially very versatile precursors for a large variety of new organometallic species. For example, attempts to coordinate a second transition metal to the free diene fragment in **22a** are described in Chapter VI. Moreover the substitution of one or more carbonyl ligands and the selective cleavage of the Sn-Ph bond in the complexes **22** are being investigated.

The synthesis and study of the fluxional nature of related η^3-cycloheptatrienyl complexes is certainly of importance in view of our attempts to unveil the relationships that might exist between the structural and fluxional parameters of these interesting compounds.

CHAPTER THREE

MISCELLANEOUS REACTIONS OF $[(C_7H_7)Fe(CO)_3]^-$.

INTRODUCTION

In this chapter some additional reactions of anion 16 will be discussed. These reactions were initiated in order to extend the known reactivity of the anion toward main group and transition metal electrophiles.

Many transition metal compounds are potential candidates to undergo a simple metathesis reaction with the potassium salt of anion 16. In view of the moderate nucleophilicity and the reducing properties of 16 the number of useful synthetic pathways is somewhat restricted. For example, the interactions of this anion with $(OC)_4$-Mn(THF)Br, $(OC)_3Re(THF)_2Br$, and $[Rh(CO)_2Cl]_2$ resulted in heterodimetallic derivatives of the type $(OC)_yM(C_7H_7)$-$Fe(CO)_3$, y = 2, M = Rh (33a), and y = 3, M = Mn (33b), or Re (33c), but very low yields were obtained.[112] Also the reaction of $(C_5H_5)Fe(CO)_2Cl$ with 16 did not lead to the product expected on the basis of the above results.[152] In most cases the dimeric complex $(OC)_3Fe(C_7H_7$-$C_7H_7)Fe(CO)_3$ was observed in varying amounts.[112,152]

In this chapter our results on the reactivity of 16 towards Ph_2PCl, $[(OC)_2W(NO)(THF)Br]_2$, and Ph_3PAuCl will be reported.

a. Reaction of $[(C_7H_7)Fe(CO)_3]^-$ with PPh_2Cl.

The reaction of 16 with PPh_2Cl was hoped to proceed according to equation (24). The product of the reaction

$$K^+[(C_7H_7)Fe(CO)_3]^- + PPh_2Cl \longrightarrow (\eta^4\text{-}7\text{-}Ph_2PC_7H_7)Fe(CO)_3 + KCl \qquad (24)$$

would be a potentially interesting new ligand system. This novel moiety would be able to act as a two-electron donor to a metal center *via* the lone pair of the phosphorous atom or possibly as a bidentate ligand by the additional involvement of the free double bond. Robertson *et al.*[153] have described the ligand 2-vinylphenyl(diphenyl)-phosphine which can act as a monodentate P-bonded or as a bidentate ligand in mononuclear carbonyl complexes of iron and ruthenium.[153] Related compounds have been reported recently by Rybinskaya and co-workers.[158] Such a bidentate ligand could have a significant influence upon the apparent 1,3-shift exhibited by the tricarbonyliron moiety in substituted (η^4-cycloheptatriene)tricarbonyliron complexes, as discussed in the previous Chapter.

Results and Discussion

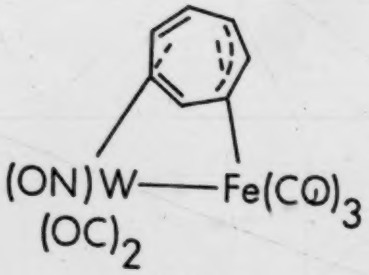
From the reaction of $\underset{\sim}{16}$ with diphenylchlorophosphine in THF at zero or ambient temperature a yellow powder could be isolated upon extraction of the crude reaction product with pentane. In hydrocarbon solutions this solid exhibited six carbonyl stretching frequencies at 2047, 2028, 1986, 1974, 1964, and 1936 cm^{-1}. The ^1H NMR spectrum showed resonances at δ (ppm): 2.4(t), 3.1(m), 3.4(m), 4.2(t), 4.5(t), 4.8-5.6(m), and 6.1(m). These complex chemical shift values and the infrared data indicated the presence of a mixture of compounds. By comparison with the spectra of an authentic sample the resonances at δ 3.1 and 4.8-5.6 were readily assigned to the dimer $[(C_7H_7)\text{-}Fe(CO)_3]_2$. The residual intensities at these δ-values and the other resonances in the spectrum constitute a pattern which is quite similar to that observed for the ring-substituted compounds $(\eta^4\text{-}C_7H_7MR_3)Fe(CO)_3$ described in Chapter II, and on this basis the second component of the mixture was tentatively identified as the ring substituted complex $(\eta^4\text{-}C_7H_7PPh_2)Fe(CO)_3$. This compound and the dimeric coupling product $\underset{\sim}{23}$ are present in approximately equal amounts, based on ^1H NMR and infrared spectral results. The formation of $\underset{\sim}{23}$ as a byproduct in this reaction also explains the large number of carbonyl stretching frequencies observed in the infrared spectrum. The bands at 2047, 1986, and 1974 cm^{-1} can be assigned to this dimer,[55] and the three remaining ν_{CO} values are then due to the species $(\eta^4\text{-}C_7H_7PPh_2)Fe(CO)_3$. The positions of the carbonyl stretching frequencies in this novel complex at 2028, 1964, and 1936 cm^{-1}, are 30-40 cm^{-1} lower than in $(C_7H_8)Fe(CO)_3$ and this is indicative of the stronger electron-releasing ability of the new ligand. Mass spectral data also support the presence of $(\eta^4\text{-}C_7H_7PPh_2)Fe(CO)_3$. Peaks are observed at m/e values of 416 (P^+), 388 ($P\text{-}CO^+$), 370, 360 ($P\text{-}2CO^+$), 332 ($P\text{-}3CO^+$, base peak), 278, 276, 183, 147 ($C_7H_7Fe^+$), 108 (PhP^+), and 91 ($C_7H_7^+$). Again the initial loss of three carbonyl groups from the parent ion forms the dominant breakdown pathway. The cluster centered at m/e 370 is tentatively assigned to $Ph_2P\text{-}PPh_2^{+}$.

The formation of 23 was also observed in Chapter II where 23 was a byproduct in the synthesis of the ring substituted species 21. Upon the work-up of these reactions the desired product could be purified by fractional crystallization, sublimation or chromatography. Fractional crystallization from hexane did not yield pure $(\eta^4\text{-}C_7H_7PPh_2)\text{-}Fe(CO)_3$. Chromatography and sublimation techniques also failed to separate the two components of the present mixture. The formation of the dimeric species indicates the partial oxidation of anion 16. The reducing power of $[(C_7H_7)Fe(CO)_3]^-$ and the complications which can arise from the electron transfer reaction in addition to the desired metathetical exchange reaction are again exemplified in this synthesis. The observation of a m/e value attributable to $Ph_2P\text{-}PPh_2$ complements the electron transfer reaction, equation (25).

$$16 + PPh_2Cl \begin{cases} \xrightarrow{\text{i}} (\eta^4\text{-}C_7H_7PPh_2)Fe(CO)_3 \\ \xrightarrow{\text{ii}} [(\eta^4\text{-}C_7H_7)Fe(CO)]_3 + Ph_2P\text{-}PPh_2 \end{cases} \qquad (25)$$

b. Reaction of $[(C_7H_7)Fe(CO)_3]^-$ with $[W(CO)_2(NO)(THF)Br]_2$.

A transition metal complex which seems well qualified to form a metal-metal bonded species upon interaction with 16 is $[W(CO)_2(NO)(THF)Br]_2$. This compound is readily prepared from $W(CO)_4(NO)Br$ by stirring the latter overnight in tetrahydrofuran at ambient temperature.[154a] As observed on several occasions, transition metal carbonyl complexes containing one or more nitrosyl groups bound to the central metal atom exhibit rather labile carbon monoxide ligands.[154] This is in line with current bonding theories in which NO acts as a stronger π-acceptor than CO and thus reduces the strength of the metal-carbonyl bond.[154a,c] It was anticipated that the coordinated THF molecule could be replaced by stronger π-bonding ligands.[154a] Interaction of this complex with 16 could thus lead to the formation of a complex like 34. The starting tungsten complex can be considered to be ready to accept five electrons from its iron counterpart upon the replacement of the halide and the coordinated solvent molecule, a feature already mentioned to be of great advantage in



34

forming heterodimetallic complexes of which 34 would be an example.[112] Both metal centers then obey the 18-electron rule. The possible ambivalent character of the nitrosyl ligand as a linear three electron or a bent one electron donor,[155] and the relevance of this feature to induce potential catalytic activity in $\underset{\sim}{34}$, added an extra stimulus to investigate this reaction.

Results and Discussion

The addition of a dichloromethane* or THF solution of $PPN^+[(C_7H_7)Fe(CO)_3]^-$ to a solution of $[W(CO)_2(NO)(THF)Br]_2$ in the same solvent did result in a reaction, as evidenced by the disappearance of the original carbonyl and nitrosyl stretching frequencies. New bands, both carbonyl and nitrosyl, were also seen in the infrared spectrum. The isolation of materials from the residue after solvent removal however proved very difficult. From chromatography on alumina, a separation technique successfully used before with other heterodimetallic complexes, a small amount of red solid could be isolated and was partly characterized by infrared and ^1H NMR spectroscopy and mass spectrometry. However, no definite conclusion about its composition could be reached.

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*Reactions of nitrosyl-containing transition metal complexes often proceed with less decomposition and/or side-reactions in dichloromethane.[154]

The infrared spectrum of this material exhibited five terminal carbonyl stretching frequencies at 2052(s), 1988(s), 1977(s), 1925(s), and 1901(s) cm^{-1}, while there is no infrared evidence for the presence of nitrosyl or bridging carbonyl ligands. The mass spectrum indicated the presence of *at least* six carbonyl ligands, the C_7H_7 unit, and W and Fe atoms. Table XVI shows a listing of the observed m/e-values. The highest m/e-value of 590 corresponds to an ion with the composition $(C_7H_7)_2WFe(CO)_6$. The successive loss of carbonyl ligands from this ion is an important breakdown pathway. Ions assignable to the ditropyl ion, $C_{14}H_{14}W^+$, and $C_{14}H_{14}Fe^+$ are also observed. The ^1H NMR spectrum of this compound shows resonances at δ(ppm) 2.96(m, ~3H), 5.11(d), 5.38(m), and 5.59(t or dd) (the last three resonances correspond to ~4H). This pattern is too complicated for fluxional cycloheptatrienyl ligands, even if the limiting spectrum is being observed. Deganello *et al.* have reported the ^1H NMR spectra of the mixed metal carbonyl ditropylium complexes $(OC)_3Fe(C_7H_7-C_7H_7)M(CO)_3$, M = Cr, Mo, and W [55] and we have also mentioned the persistent presence of the M = Fe complex in many of the reactions of anion $\underset{\sim}{16}$. The ^1H NMR spectra of the mixed complexes do not fit the present results even though the mass spectra appear to support such an assignment. Although the NMR spectrum closely resembles that of the Fe-Fe complex, the present

TABLE XVI

Mass spectral data of the red compound isolated from the reaction of $[(C_7H_7)Fe(CO)_3]^-$ with $[W(CO)_2(NO)(THF)Br]_2$.[a,b]

Assignment (tentative)	m/e			rel. abundance (%)
$(C_7H_7)_2WFe(CO)_6^+$	590			1.1
$(C_7H_7)_2WFe(CO)_5^+$	562			38.9
$(C_7H_7)_2WFe(CO)_4^+$	534			5.9
$(C_7H_7)_2WFe(CO)_3^+$	506			32.2
$(C_7H_7)_2WFe(CO)_2^+$	(480)	478[c]	(16.7)	16.4
$(C_7H_7)_2WFe(CO)^+$ *or* $(C_7H_7)_2W(CO)_3^+$	(452)	450[c]	(16.5)	16.1
$(C_7H_7)_2WFe^+$ *or* $(C_7H_7)_2W(CO)_2^+$	422			28.5
-	398			4.3
$(C_7H_7)_2W(CO)^+$	394			3.3
$(C_7H_7)_2W^+$	366			16.1
$(C_7H_7)FeW(CO)^+$ *or* $(C_7H_7)W(CO)_3^+$	359			100.0
$(C_7H_7)WFe^+$ *or* $(C_7H_7)W(CO)_2^+$	331			32.3
$(C_7H_7)W(CO)^+$	303			7.1
$(C_7H_7)_2Fe(CO)_2^+$	294			29.6
$(C_7H_7)_2Fe(CO)^+$	266			17.4
$(C_7H_7)_2Fe^+$	238			40.3
-	203			8.8

continued....

TABLE XVI (Continued)

$(C_7H_7)_2^+$	182	6.8
–	160	20.5
$(C_7H_7)Fe^+$	147	32.8
$(C_6H_6)Fe^+$	134	7.8
$(C_7H_8)^+$	92	24.5
$(C_7H_7)^+$	91	56.6

[a] Not corrected for ^{13}C; all m/e-values correspond to the ions containing the ^{184}W-isotope; m/e-values > 91 are reported.

[b] 18 eV, 160°C.

[c] Although the intensities of these ions are very similar, the W-isotope pattern is disturbed within this cluster. The natural abundancy of the ^{186}W-isotope is smaller than that of the ^{184}W-isotope.

complex is red whereas the Fe-Fe compound is yellow. It appears that a mixture of compounds is present with, on basis of the ^1H NMR spectra, the Fe-Fe dimer as the major component. The mixed Fe-W carbonyl complex is possibly present as a second species.

The synthetic applicability of $[(C_7H_7)Fe(CO)_3]^-$ in the synthesis of nitrosyl containing polynuclear complexes thus appears to be less straightforward than its use in the synthesis of dinuclear transition metal carbonyl compounds. Considerable experimental difficulties are to be expected in the synthesis of such complexes *via* the anion $\underset{\sim}{16}$ as the compounds employed so far failed to yield isolable nitrosyl containing dimetallic species.*

c. Reactions of $[(C_7H_7)Fe(CO)_3]^-$ with $Au(PPh_3)Cl$.

The impetus for considering the interaction of $\underset{\sim}{16}$ with $Au(PPh_3)Cl$ originated from the analogous behaviour observed for $Au(PPh_3)Cl$ and Ph_3SnCl towards transition metal carbonyl anions. In particular, Ellis has shown that both compounds are equally well suited to characterize highly reduced anions.[156] In an isolated case, e.g. in the characterization of $Mn(CO)_4^{3-}$,[156c] Ph_3PAuCl fulfills this task even better than Ph_3SnCl due to the reduced crowding around the gold atom. Our successful synthesis of metal-metal bonded species with Ph_3SnCl and Ph_3PbCl prompted us to attempt the synthesis of $(C_7H_7)Fe(CO)_3(AuPPh_3)$, equation (26). The formation of an interesting complex containing

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*$Mo(NO)_2Cl_2$ also did not yield an identifiable nitrosyl containing complex in its reaction with $\underset{\sim}{16}$.[160]

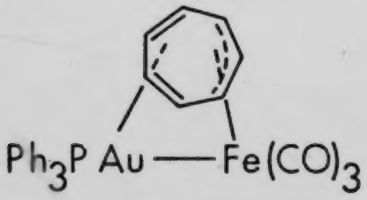
$$[(C_7H_7)Fe(CO)_3]^- K^+ + Ph_3PAuCl \longrightarrow (\eta^3\text{-}C_7H_7)Fe(CO)_3AuPPh_3 + KCl \tag{26}$$

an iron to gold metal-metal bond was expected. The general interest in, and the emphasis presently placed upon, metal-metal bonded compounds with respect to e.g. homogeneous catalysis has recently been reviewed.[157]

Results and Discussion

The first addition of a THF solution of 16 to a similar solution of $AuPPh_3Cl$ formed the beginning of a long series of experiments. Based upon the similarity between Ph_3SnCl and Ph_3PAuCl [156] a "smooth" reaction was expected to give $(\eta^3\text{-}C_7H_7)Fe(CO)_3AuPPh_3$ in good yield. But, as the experimental proceedings will show, this reaction proved to be much less well behaved than the analogous reactions with triphenyltin and triphenyllead chloride. Upon extraction of the crude reaction product with toluene and cooling of the obtained solution at 4°C a red oil resulted. Infrared spectra showed six terminal carbonyl stretching frequencies at 2047(s), 2034(sh), 2006(s), 1973(s,br), 1924(s), and 1900(m) cm^{-1}. Removal of the supernatant and addition of varying amounts of dichloromethane, toluene and/or hexane with appropriate cooling and/or concentrating of the obtained mixtures failed to produce a crystalline material. Often a brown precipitate would result while a thin layer of, presumably, metallic gold would be deposited on the walls of the container. One component of this precipitate could be identified by its infrared and mass spectra as $(Ph_3P)_2Fe(CO)_3$.

One particular reaction produced a small amount of a red solid which analyzed well for $(C_7H_7)Fe(CO)_3AuPPh_3$. The ^1H NMR spectrum in CD_2Cl_2 of a similar but less pure sample showed a sharp resonance for the cycloheptatrienyl protons at δ 5.16 ppm, as expected for a fluxional η^3-C_7H_7 group. Interestingly, this signal did not broaden significantly between +30 and -90°C. At lower temperatures the resonance broadened and collapsed into the baseline at ~-130°C. This is a dramatic increase in fluxionality when compared to the complexes 22a and 22b where the coalescence temperatures were observed at ~-60°C and ~-65°C, respectively. In light of these ^1H NMR data and the correct elemental analysis we believe that the compound $(C_7H_7)Fe(CO)_3AuPPh_3$ has been synthesized. However the low coalescence temperature of the C_7H_7 ligand observed in this complex is difficult to reconcile with the simple structural form 22. We have noted before that the attachment of a second metal carbonyl moiety in a cisoid fashion to the cycloheptatrienyl ring results in greatly enhanced fluxional behaviour compared to the mononuclear complexes. Based on this experimental observation we are tempted to propose the structure shown below, 35, for the Fe-Au complex. In the proposed structure



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both metal atoms achieve an 18-electron configuration. The compound would also be an example of the coordination of gold(I) to an unsaturated organic moiety. Very few examples are known in which Au(I) is π-bonded to an organic moiety.[161] Moreover, the stability of π-complexes of Au(I) is rather low and the reversible addition of unsaturated ligands is possible in some cases.[161]

Conclusions

The reactivity of anion 16 towards PPh_2Cl, $[W(CO)_2(NO)(THF)Br]_2$, and $AuPPh_3Cl$ proved to be much more complicated than the reactions of $[(C_7H_7)Fe(CO)_3]^-$ with group IV electrophiles. In each case a metathetical exchange reaction was envisaged which would lead to a novel and interesting species worthwhile of further investigation.

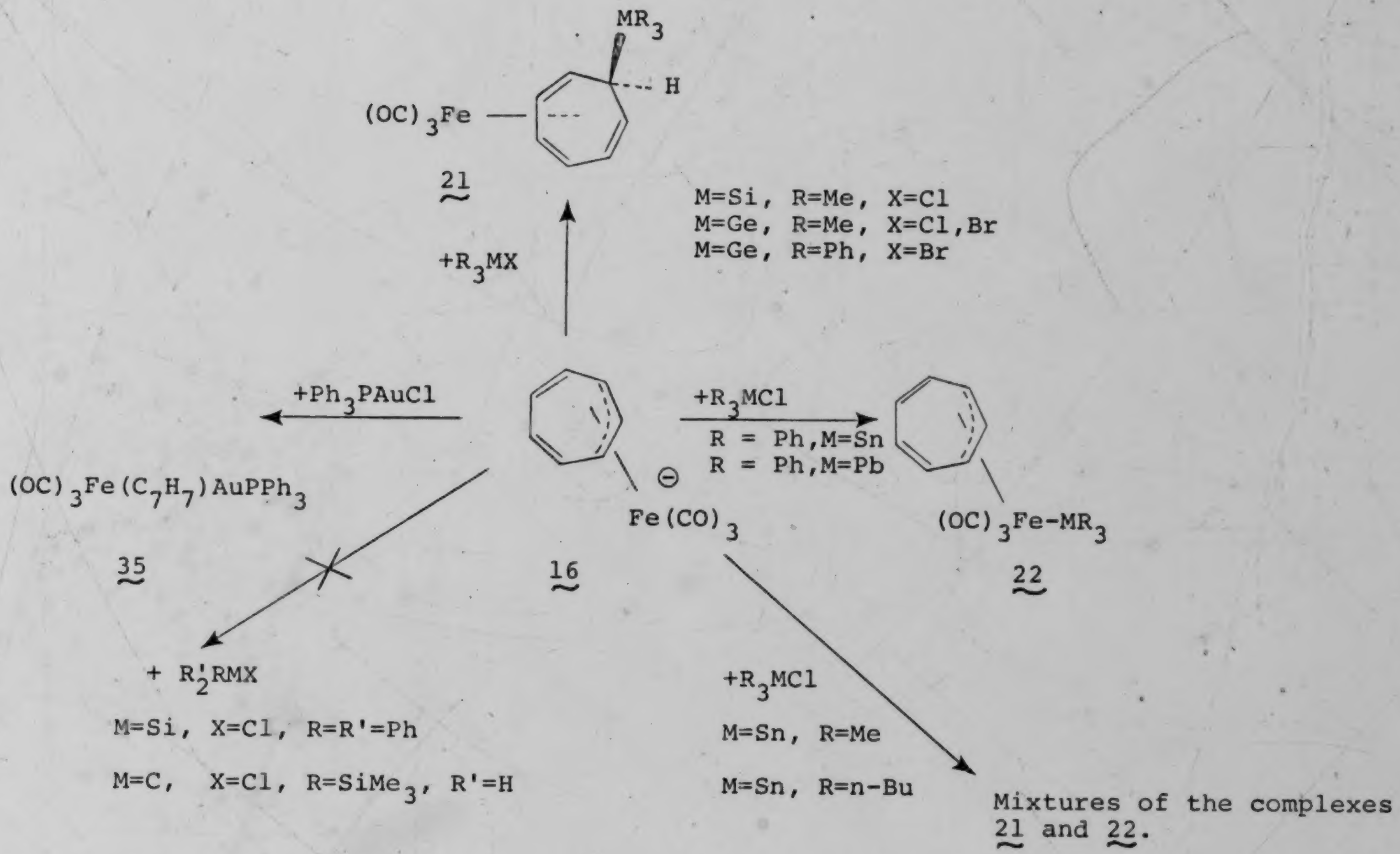
From the reactions of 16 with Ph_2PCl and $AuPPh_3Cl$ evidence was obtained that the complexes $(\eta^4\text{-}C_7H_7PPh_2)\text{-}Fe(CO)_3$ and $(C_7H_7)Fe(CO)_3AuPPh_3$ had indeed been formed.

However difficulties were encountered in all attempts to isolate the pure compounds. For example, ^1H NMR, infrared, and mass spectral data indicated the presence of the complex $(\eta^4\text{-}C_7H_7PPh_2)Fe(CO)_3$ but no pure crystalline or solid material could be obtained. It followed from the identification of $[(C_7H_7)Fe(CO)_3]_2$ as a by-product that partial oxidation of anion $\underset{\sim}{16}$ had occurred during the course of the reaction. A competing electron transfer reaction was therewith inferred. Severe difficulties in obtaining a pure sample were also encountered in the reaction of $\underset{\sim}{16}$ with $AuPPh_3Cl$. Decomposition prevailed and $(Ph_3P)_2Fe(CO)_3$ was observed as one of the reaction products. A tiny amount of red solid was isolated which analyzed correctly for $(C_7H_7)Fe(CO)_3AuPPh_3$. The variable temperature ^1H NMR spectra of a similar sample showed that the fluxional proxess, which is responsible for the equivalence of the cycloheptatrienyl protons on the NMR time-scale, is surprisingly facile. This is compatible with the presence of a cis-heterodinuclear cycloheptatrienyl complex in which both metal atoms are coordinated to the bridging cycloheptatrienyl ligand. Further efforts are continued in order to obtain a crystalline sample of this compound suitable for crystallographic analysis.

We could not isolate a nitrosyl containing dinuclear compound from the interaction of $\underset{\sim}{16}$ with $[W(CO)_2(NO)(THF)Br]_2$. Only a small amount of red crystalline material was obtained and characterized by infrared and ^1H NMR spectroscopy and and mass spectrometry. Mass spectral data tend to support the formulation of this compound as $(C_7H_7)_2WFe(CO)_6$; however, the ^1H NMR data show the presences of mainly the Fe-Fe dimeric complex $\underset{\sim}{23}$.

Although many experimental difficulties were encountered in the above reactions some clear indications as to the course of these reactions and the nature of the products formed could be extracted. Unfortunately, they continue to pose an interesting challenge to the synthetic organometallic chemist.

The known reactivity of $[(C_7H_7)Fe(CO)_3]^-$ is summarized in Scheme VI.


MR$_3$
H
(OC)$_3$Fe
21
+R$_3$MX
M=Si, R=Me, X=Cl
M=Ge, R=Me, X=Cl,Br
M=Ge, R=Ph, X=Br
+Ph$_3$PAuCl
(OC)$_3$Fe(C$_7$H$_7$)AuPPh$_3$
35
⊖
Fe(CO)$_3$
16
+R$_3$MCl
R = Ph,M=Sn
R = Ph,M=Pb
(OC)$_3$Fe-MR$_3$
22
+ R'$_2$RMX
M=Si, X=Cl, R=R'=Ph
M=C, X=Cl, R=SiMe$_3$, R'=H
+R$_3$MCl
M=Sn, R=Me
M=Sn, R=n-Bu
Mixtures of the complexes 21 and 22.

Scheme VI. Summary of the reactivity of the anion $[(C_7H_7)Fe(CO)_3]^-$, as described in the Chapters II and III.

CHAPTER FOUR

ENDO-DEPROTONATION OF (η^4-exo-7-$Ph_3GeC_7H_7$)Fe(CO)$_3$ AND REACTIVITY OF THE ANION [($Ph_3GeC_7H_6$)Fe(CO)$_3$]$^-$.

INTRODUCTION

Proton abstraction from an organic ligand coordinated to a transition metal is beginning to emerge as a useful route towards the synthesis of anionic organometallic complexes and frequently forms the initial step in the formation of new neutral organometallic species.[165] Furthermore, such deprotonation and subsequent electrophilic attack can provide a convenient entry into a group of otherwise inaccessible organic molecules upon removal of the organic substrate from the metal. Synthetic procedures to accomplish this latter task under rather mild conditions have recently been developed.[159,166]

However, in all instances reported to date the abstraction of a proton from an organic moiety coordinated to a metal occurs *exo* to the transition metal center. The proton is removed from the face of the organic ligand opposite the face occupied by the transition metal.[105,106,165c]

Exo-deprotonation of cycloheptatrienetricarbonyliron occurs to give the anion [(C_7H_7)Fe(CO)$_3$]$^-$. In the previous chapters we have described the reactivity of this anion towards transition metal and main group electrophiles and demonstrated its versatility in the synthesis of novel, fluxional organometallic compounds. One particular type of complexes synthesized are represented by the general formula (η^4-$R_3MC_7H_7$)Fe(CO)$_3$, complexes $\underset{\sim}{21}$ with M = Si, Ge.

These compounds, for which an *exo*-configuration of the R_3M group was established by a crystallographic structure determination for 21b, are stereochemically non-rigid. The mechanism of the process responsible for the time-dependent NMR spectra was identified as an oscillatory motion of the $Fe(CO)_3$ moiety with respect to the ring, corresponding to an apparent 1,3-shift.

In this Chapter we will discuss the synthesis of the anion $[(C_7H_6GePh_3)Fe(CO)_3]^-$, 36, from the action of t-BuOK upon $(Ph_3GeC_7H_7)Fe(CO)_3$, 21c, in tetrahydrofuran. During the course of our work Behrens and co-workers have reported that $(7\text{-}MeOOCC_7H_7)Fe(CO)_3$ also can be deprotonated*.[74] The formation of these anions constitutes the first examples of the abstraction of an *endo*-proton from a coordinated organic moiety in an organometallic compound.

Results and Discussion

a. Synthesis

Addition of a solution of $(7\text{-}Ph_3GeC_7H_7)Fe(CO)_3$ in tetrahydrofuran to a slurry of t-BuOK in tetrahydrofuran, at ambient temperature, results in the formation of a very air-sensitive deep red solution. The infrared spectrum of this solution exhibits two carbonyl absorption bands

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[*] The stereochemistry of this reaction has not been investigated. Moreover the complex $(7\text{-}MeOOCC_7H_7)Fe(CO)_3$ rearranges rapidly, particularly in the presence of base, to the $(6\text{-}MeOOCC_7H_7)Fe(CO)_3$ isomer.[74]

at 1938 and 1864 cm^{-1}, indicating the conversion of the starting material into an anionic carbonylate complex. The values of these frequencies are similar to those of the unsubstituted anion (1942 and 1868 cm^{-1}). Upon removal of the solvent from this solution *in vacuo*, a red solid is obtained. In order to improve on the air stability and solubility of the complex we have attempted to prepare the bis(triphenylphosphine)iminium salt.[167] Addition of an equimolar amount of PPNCl [167] to the red THF solution resulted in the partial exchange of the potassium ion by the bis(triphenylphosphine)iminium ion. Identical NMR spectra were obtained for each solid. The PPN^+ stabilized anion $[(C_7H_6GePh_3)Fe(CO)_3]^-$ is however slightly less prone towards decomposition.

b. NMR Spectral data.

The C.W. ^1H (100 MHz) NMR spectrum of $\underset{\sim}{36}$ is shown in Figure XXXII ($3.0 \leqslant \delta \leqslant 6.5$), also shown are the results of the selective irradiation of the resonances at δ 4.03 (1,1'), 4.88(3,3'), and 6.17(2,2'), respectively. The assignment of the three resonances follows from the decoupling experiments. Figure XXXIII shows both the experimental FT ^1H (100 MHz) NMR spectrum and the calculated spectrum obtained by computer simulation. The values extracted for the coupling constants are also indicated in Figure XXXIII. The spectrum at ambient temperature

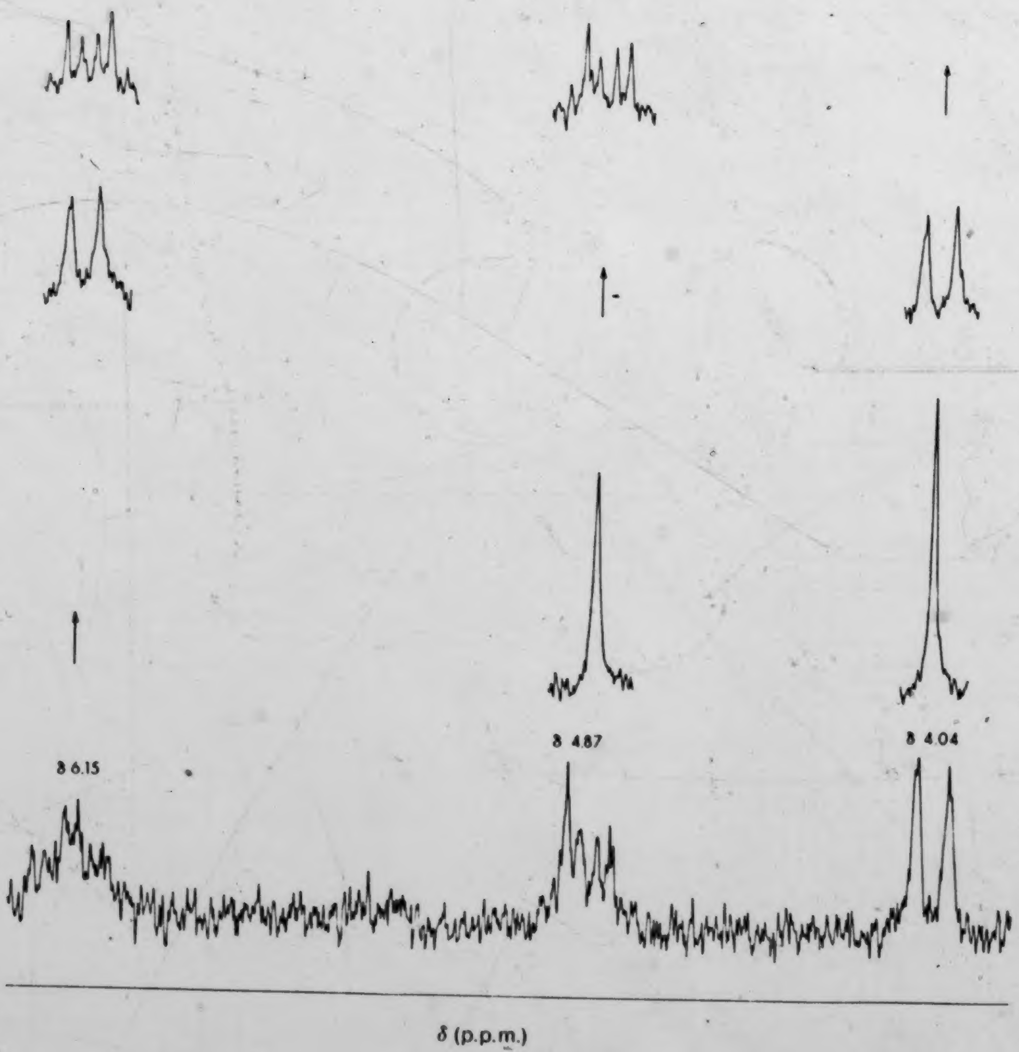
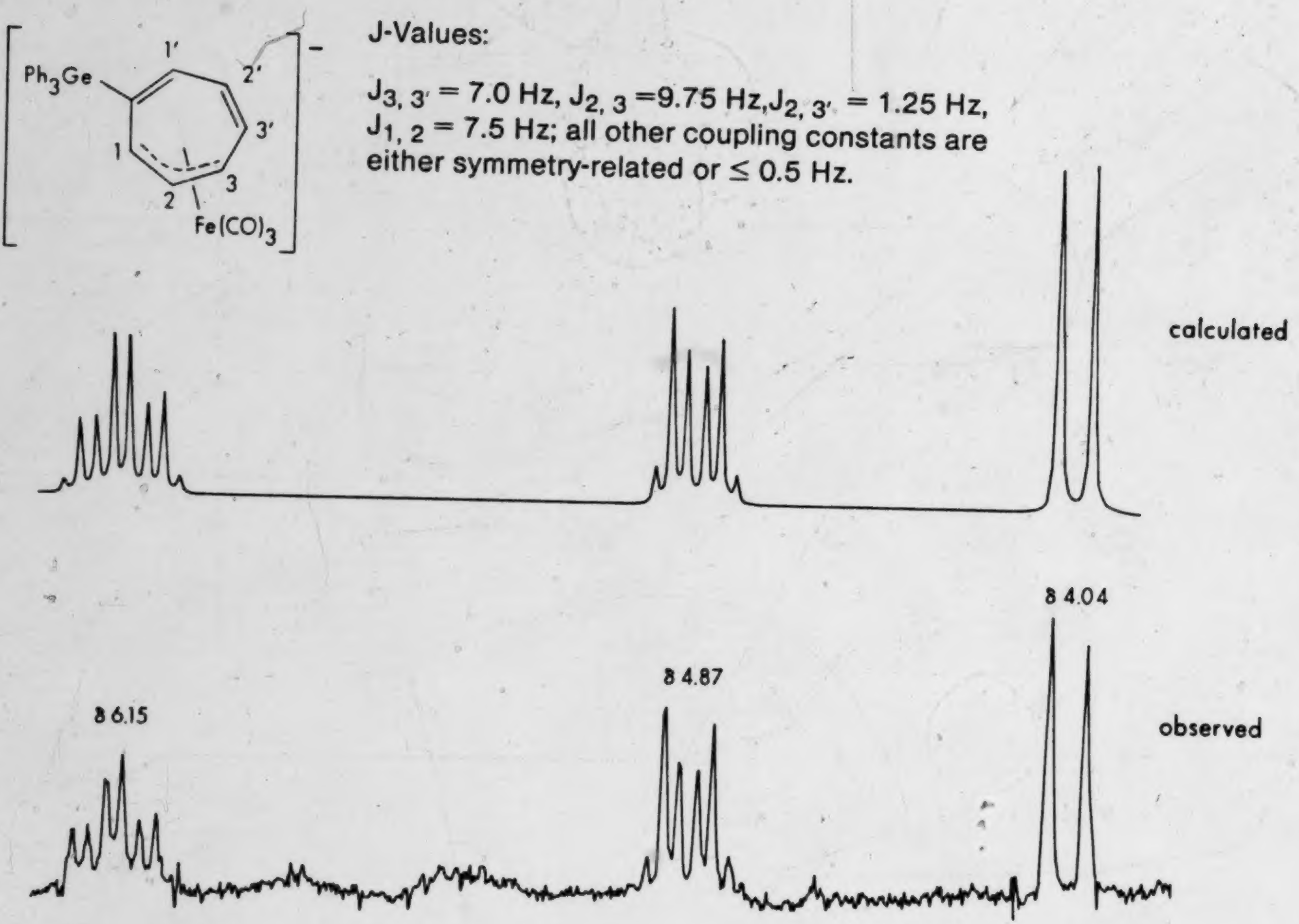


Figure XXXII. C.W. ^1H NMR Spectra of $[(C_7H_6GePh_3)-Fe(CO)_3]^-$ in THF-d_8 and Selective Decoupling Experiments.

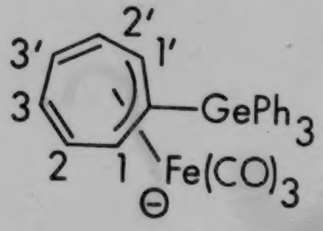


J-Values:

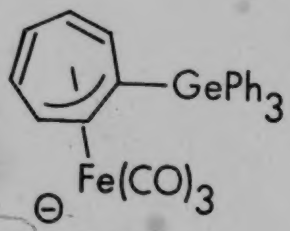
$J_{3,3'}$ = 7.0 Hz, $J_{2,3}$ =9.75 Hz,$J_{2,3'}$ = 1.25 Hz, $J_{1,2}$ = 7.5 Hz; all other coupling constants are either symmetry-related or ≤ 0.5 Hz.

Figure XXXIII. F.T. ^{1}H and Calculated Spectra of $[(Ph_3GeC_7H_6)Fe(CO)_3]^-$.

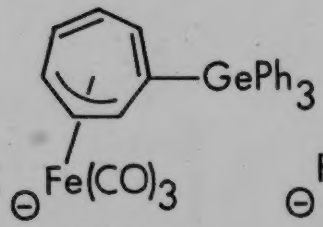
would be consistent with a symmetrical structure 36a, or its diene counterpart, for the anion but it more likely constitutes a time average of 36a-36d. The averaging



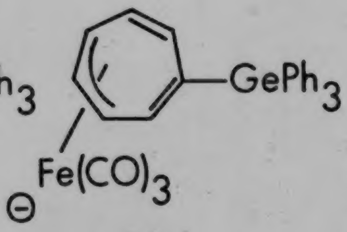
36a



36b



36c



36d

process being the result of rapid ring-whizzing executed by the $Fe(CO)_3$ moiety in the form of fast, consecutive 1,2-shifts, accompanied by simultaneous electronic redistributions, with either the predominance of one most stable bonding mode at all temperatures or the presence of an equilibrium mixture of forms 36a-36d, which in addition could be temperature dependent.*

In the ^1H NMR spectra of the unsubstituted parent ion $[(C_7H_7)Fe(CO)_3]^-$ a sharp resonance is observed for the cycloheptatrienyl hydrogens at temperatures above -100°C at δ 4.90 ppm. Only upon further cooling does the resonance broaden and finally disappear into the baseline at T $\cong$ -140°C (Chapter I). The low temperature limiting spectrum could not be obtained even at -165°C. It was not unreasonable to expect that the introduction of a sterically demanding substituent like $(C_6H_5)_3$Ge would increase the free energy of activation of the rearrangement process and thereby render this substituted anion more amenable for a study of its variable temperature ^{1}H and ^{13}C NMR profiles.[68] The question whether the solution structure of anion 36 is best represented by an η^3-allyl or an η^4-diene coordination mode, forms 36a-36d and 36e-36h respectively,

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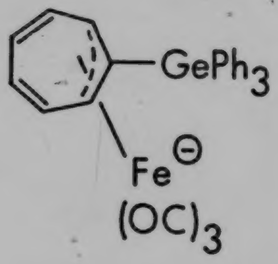
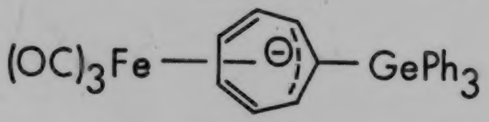
*Similar structures can be written for the coordinated diene counterparts, 36e-36h.



36a - 36d



36e - 36h

might then be resolved. Unfortunately, due to the decreased stability of 36, relative to 16, in chlorinated solvents, only THF-d_8 could be applied as a low temperature solvent. As a result the temperature range available was further restricted. Very little change occurred in the ^{1}H NMR spectra between ambient temperature and -90°C. The slight broadening which was observed might well be due to the increased viscosity of the solution at -90°C. The variable temperature ^{13}C NMR studies however showed that the spectra observed at ambient temperature are the result of a temperature dependent process. The resonances broadened and collapsed into the baseline upon lowering the temperature, T_c being approximately -60°C. The low temperature limiting spectrum could still not be observed at -90°C. The effect of the triphenylgermyl substituent on the ring-whizzing motion executed by the $Fe(CO)_3$ unit is thus not large enough to increase the coalescence temperature to the point that extraction of the activation parameters becomes possible. We will return to the question of the solution structure of **36** after discussing certain aspects of its reactions with electrophiles.

c. Reactivity of the anion $[(Ph_3GeC_7H_6)Fe(CO)_3]^-$.

1. Reactions with Me_3SiCl and Ph_3SnCl.

The anion $[(Ph_3GeC_7H_6)Fe(CO)_3]^-$ displays an interesting chemistry to which we now direct our attention. It was shown in previous Chapters that the anion **16** can react with a variety of electrophiles to give two different classes of reaction products. It was then of interest to compare the reactivity of **36** to that of **16** in order to see whether the same ambident nucleophilic character will be exhibited by anion **36** also. As will be seen, the reactivity of **36** is related to that of **16** but different in some aspects.

Upon addition of the red substituted anion to a solution of trimethylchlorosilane in THF rapid decolouration occurred. The resulting yellow reaction mixture yielded, after work up, a small amount of a yellow solid which was identified by ^1H and ^{13}C NMR spectroscopy and mass spectrometry as the substituted dimeric complex $[(C_7H_6GePh_3)Fe(CO)_3]_2$, $\underset{\sim}{37}$. No ring-disubstituted products could be isolated,* while $(C_7H_8)Fe(CO)_3$ was identified as a product by infrared spectroscopy. The highest peak observed in the mass spectrum was centered at 984 and is assigned to $P-3CO^+$. A good agreement between the observed and calculated intensity ratios in the cluster was observed. The ^1H and ^{13}C NMR spectral data of the complex are collected in Table XVII. All the proton assignments were confirmed by selective decoupling experiments. Since we are dealing with a substituted ditropylcarbonyliron derivative the position of the Ph_3Ge moiety on the seven-membered ring must be determined in addition to the stereochemistry at the C(7) carbon. The observation of one set of proton and carbon resonances indicates that the substitutional pattern of each ring is identical and that the two seven membered rings are related by some symmetry operation. Based on the chemical shift values alone,

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*The only indication of the presence of a disubstituted complex came from the mass spectra of the crude solid, before crystallization, in which a cluster centered at m/e = 524 was observed, assignable to the ion $[C_7H_6GePh_3(SiMe_3)]Fe^+$.

TABLE XVII

^1H and ^{13}C NMR parameters for $[(Ph_3GeC_7H_6)Fe(CO)_3]_2$.[a]

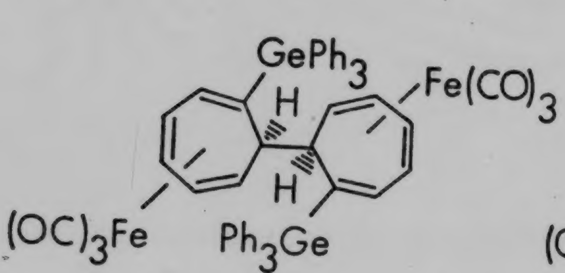
Compound		Assignment							Ph	CO	Solvent
		5	6	2	3	1	4	7			
37	^1H	6.13	-	4.48	4.58	2.73	2.54	2.28	7.00-7.80	-	C_6H_6
	^{13}C	-[b] -[b]	-[b] -[b]	88.2 + 93.4		56.5 + 61.1		33.4	129.0 - 140.5	211.7	C_6H_6

---

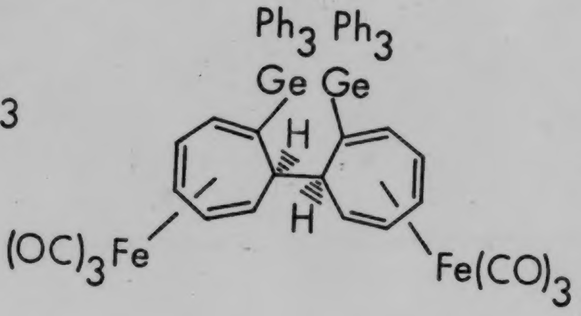
[a] Chemical shifts (δ) in ppm from TMS by appropriate conversion from internal solvent references.

[b] Carbons C(5) and C(6) are obscured by the phenyl resonances.

which show the presence of both outer and inner protons of a coordinated diene moiety, the 1,2,3, and 4 substituted isomers can be eliminated from further consideration. A choice between the 5 and 6 isomers can be secured from the coupling pattern exhibited by the molecule. The strong coupling between H(4) and the proton of the free double bond (9 Hz), the small coupling between this latter proton and H(7) (2 Hz), and the triplet appearance of H(4) due to coupling to H(3) and the proton at δ6.13 ppm all indicate the presence of the 6-Ph_3Ge isomer. As mentioned before, a delineation of the stereochemistry at C(7) based on NMR spectroscopy alone is hazardous at best. However, the relatively large coupling constant between H(1)-H(7) (5 Hz), the relatively low chemical shift value of the H(7) resonance and the deduced *exo-exo* stereochemistry of $(OC)_3Fe(C_7H_7\text{-}C_7H_7)Fe(CO)_3$,[55] obtained by oxidative coupling of $[(C_7H_7)Fe(CO)_3]^-$,[55] are more in line with *exo-exo* stereochemistry in **37** too. The two possible isomers fulfilling these requirements, C_2 and C_s symmetries, are shown below.



37a, C_2



37b, C_s

Since the C_2 isomer is free of steric interactions between the bulky Ph_3Ge substituents this isomer is postulated as the most probable ground state structure of the complex. ^{13}C NMR spectral data complement the above assignment and are also listed in Table XVII.

The isolation of only $[(C_7H_6GePh_3)Fe(CO)_3]_2$ is unlike the reaction of the unsubstituted anion $[(C_7H_7)Fe(CO)_3]^-$ with Me_3SiCl, which resulted mainly in the ring-substituted complex **21a**. The presence of an electron-releasing substituent on the ring might facilitate an electron transfer reaction, leading to dimerization. This is similar to the formation of $[(C_7H_7)Fe(CO)_3]_2$ discussed in the previous chapter. The seemingly more pronounced tendency of **36**, as compared to **16**, to undergo this reaction is noted.

The interaction of $[(C_7H_6GePh_3)Fe(CO)_3]^-$ with triphenyltin chloride led to the isolation of a small amount of a red crystalline material which was identified by ^1H NMR and mass spectral data as a mixture of $(Ph_3GeC_7H_6)$-$Fe(CO)_3SnPh_3$, **38**, and **22a**. Considerable amounts of the reactants, **21c** and Ph_3SnCl, could also be recovered. The compound **38** was obtained by crystallization from hexane, after **21c** and Ph_3SnCl had also been removed from the reaction mixture by fractional crystallization. The mass spectrum of this red solid showed, in addition to lower m/e-values, clusters centered around 828 and 800, assigned to the ions $P-2CO^+$ and $P-3CO^+$. As shown in Figure XXXIV

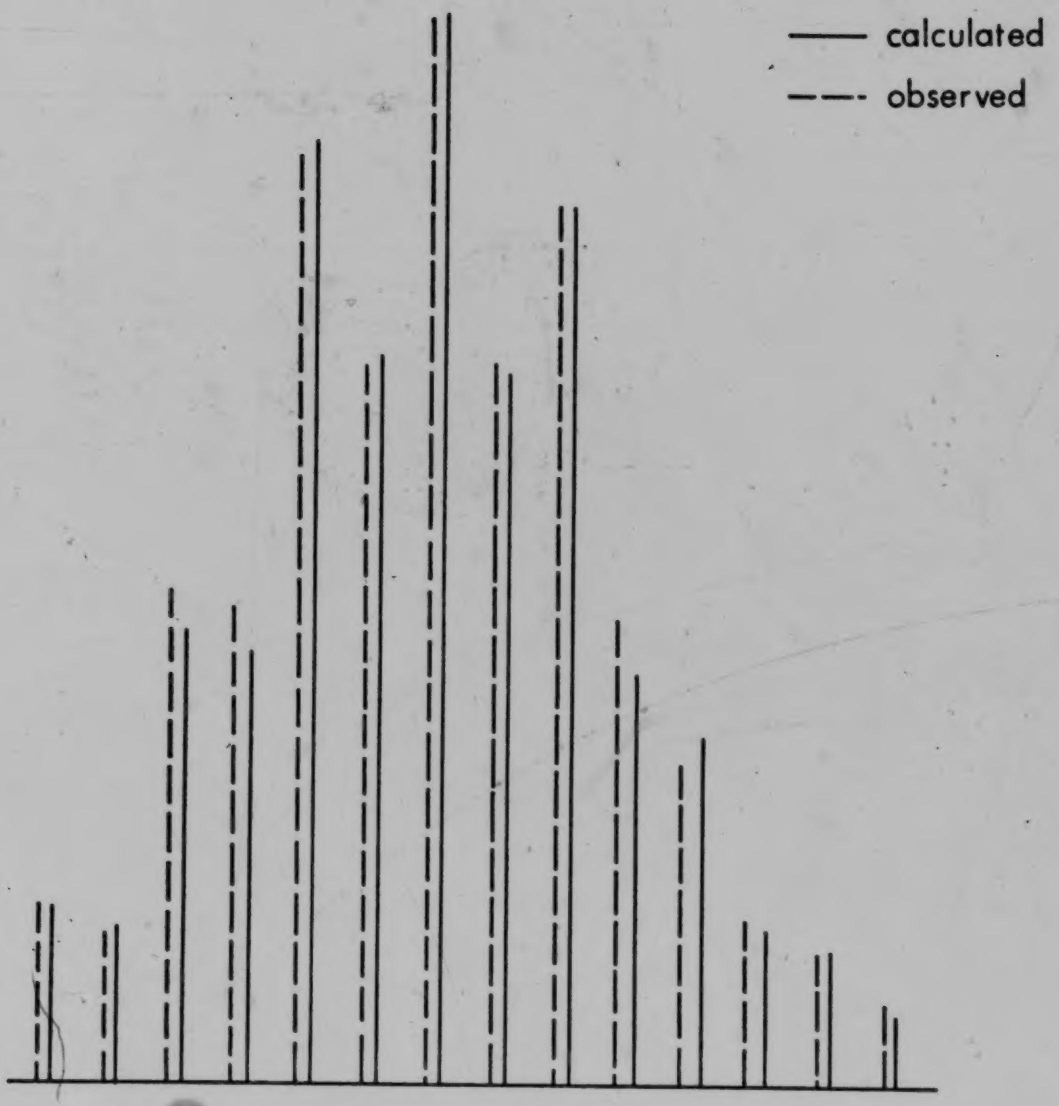
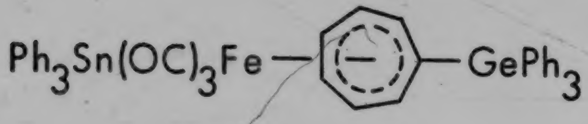


Figure XXXIV. Observed and calculated intensity ratios in the cluster assigned to $[Ph_3GeC_7H_6Fe(CO)SnPh_3]^+$.

a good agreement between the observed and calculated intensities for the peaks in the cluster at m/e 828 is found. The ^1H NMR spectrum (at 100 MHz) showed peaks at δ 4.38(1H,m), 4.69(1H, m), and 5.90(1H,d) ppm. An additional single peak is observed at δ 4.85 ppm and is assigned to the unsubstituted analog 22a. It follows from the integration ratio that an approximately 7:1 mixture of the substituted and unsubstituted compounds is present. The formation of 22a suggests that partial cleavage of the $C(sp^3)$-Ge bond in 21c occurs under the influence of t-BuOK. Behrens and co-workers have reported that the cleavage of the carbon-germanium bond is the only reaction observable in $(7\text{-}Et_3GeC_7H_7)Fe(CO)_3$ upon the action of $NaN(SiMe_3)_2$.[74] In view of the fluxional behaviour of the complexes 22 the simple NMR spectrum of 38 most probably reflects nonrigid behaviour of this compound as well. The low field doublet at δ 5.90 ppm is attributed to the 1 and 1'



38

protons which appear to experience a strong deshielding effect due to the triphenylgermyl substituent. Of course

TABLE XVIII

^{1}H and ^{13}C NMR parameters for the compounds $[(Ph_3GeC_7H_6)Fe(CO)_3]^-$ and $(Ph_3GeC_7H_6)Fe(CO)_3SnPh_3$.[a]

Compound		Assignment					Solvent
		1,1'	2,2'	3,3'	Ph	CO	
36	^{1}H	4.04	6.15	4.87	7.00-7.90	-	THF
	^{13}C	72.0	-[b]	103.9	125.8-140.2	224.3	THF
38	^{1}H	5.90	4.69	4.38	7.00-7.80	-	C_6H_6

[a] Chemical shifts (δ) in ppm from TMS by appropriate conversion from internal solvent references.

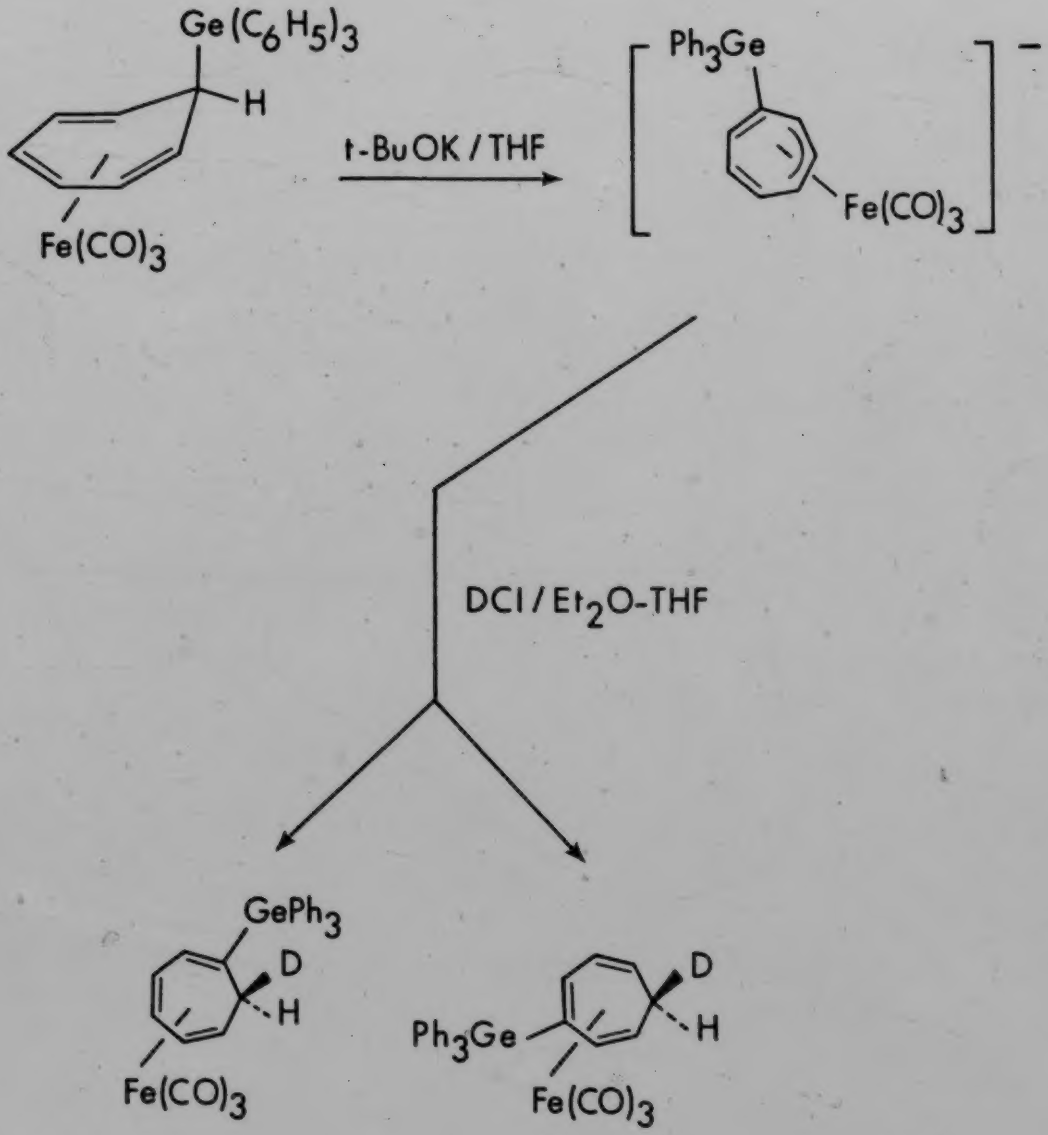
[b] Carbons C(2) and C(2') are obscured by the phenyl resonances.

its position must also reflect the limiting solution structure of the compound. Selective decoupling experiments support the assignment of the proton resonances as shown. We will return to the precise nature of the instantaneous structure after discussing the reactions of **36** with the more elementary electrophile D^+.

2. Reactions with DCl.

The addition of an equimolar quantity of deuterium chloride, dissolved in a 1:1 mixture of diethyl ether and tetrahydrofuran, to anion **36**, dissolved in tetrahydrofuran, results in a distinct colour change from red to yellow, a sharp endpoint being observed in this titration. As outlined in Scheme VII *only* two isomeric compounds could subsequently be isolated, $(3\text{-}Ph_3Ge,7\text{-}D_7CH_6)Fe(CO)_3$, **39a**, in ~66%, and $(6\text{-}Ph_3Ge,7\text{-}DC_7H_6)Fe(CO)_3$, **39b**, in ~33% relative yield. The two isomers can be separated by repeated fractional crystallization. Upon crystallization from hexane the less soluble 3-Ph_3Ge isomer is obtained first. Subsequent concentration and cooling of the mother liquor yields the less abundant 6-Ph_3Ge isomer. It is important for crystallization to occur slowly (3-4 days). Under such conditions two or three recrystallizations proved to be sufficient to obtain a complete separation of the two isomers.

The ^1H (100 MHz) NMR spectra of the complexes **39** are depicted in Figure XXXV, $2.0 \leqslant \delta$ (ppm)$\leqslant 6.5$. The proton


Ge(C6H5)3
H
Fe(CO)3
t-BuOK / THF
Ph3Ge
Fe(CO)3
DCl / Et2O-THF
GePh3
D
H
Fe(CO)3
D
Ph3Ge
H
Fe(CO)3

Scheme VII. Synthesis of $(3\text{-}Ph_3Ge,7\text{-}DC_7H_6)Fe(CO)_3$ and $(6\text{-}Ph_3Ge,7\text{-}DC_7H_6)Fe(CO)_3$.

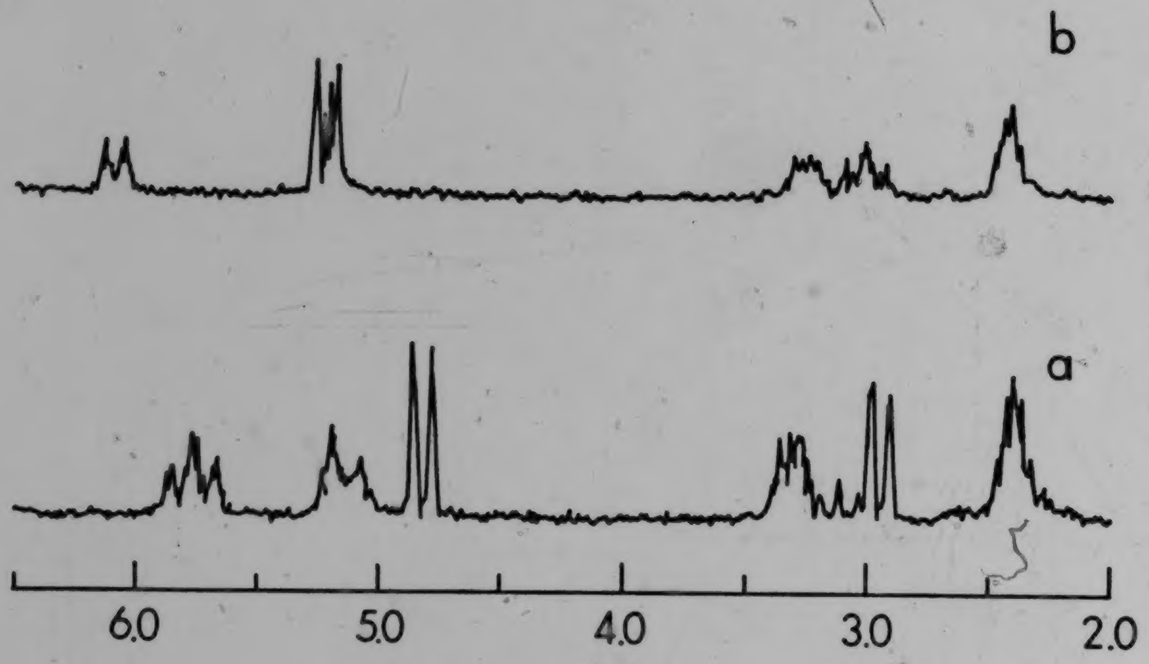


Figure XXXV. ^1H NMR spectra of $(3\text{-}Ph_3Ge,7\text{-}DC_7H_6)Fe(CO)_3$, a, and $(6\text{-}Ph_3Ge,7\text{-}DC_7H_6)$-$Fe(CO)_3$, b. $2.0 \leq \delta(ppm) \leq 6.5$ in CS_2.

NMR spectra served as a convenient method to identify the two compounds as the 3-Ph_3Ge and 6-Ph_3Ge isomers, even though the interpretation of the spectra of the initial mixture required considerable scrutiny. All assignments are supported by selective decoupling experiments and were made in a manner analogous to that outlined for complex **37**. A comparison of the ^1H NMR spectra of (C_7H_8)-$Fe(CO)_3$ and the three isomers of $(C_7H_6RGePh_3)Fe(CO)_3$, R = H or D, in Table XIX, reveals that the triphenylgermyl group can have a rather substantial deshielding effect upon the neighboring hydrogen atoms. For example, the H(1), H(6), and *endo*-H(7) protons in **21c**, and the H(5) proton in **39b** are all shifted to lower field. However, the effect is not observed for all protons which are bound to a carbon atom adjacent to the triphenylgermyl bearing carbon atom.

It is emphasized that in the complexes the deuterium atom is considered to occupy the 7-*exo* position. The assumption of *exo*-attack on **36** stems from analogous observations made by Maltz[105] and Brookhart[106] for anion **16**. The intricate coupling patterns observed within the seven-membered ring preclude the use of J-values in determining the *exo*- or *endo*-position of H(7) on the basis of the relationship between the size of the coupling constants and the dihedral angle. Moreover it was found in Chapter II that correlations based upon chemical shift

TABLE XIX

^{1}H NMR spectroscopic data for the compounds (3-Ph_3Ge, 7-DC_7H_6)$Fe(CO)_3$, (6-Ph_3Ge,7-DC_7H_6)$Fe(CO)_3$ and (7-$Ph_3GeC_7H_7$)$Fe(CO)_3$ and (C_7H_8)$Fe(CO)_3$ at ambient temperature.[a]

Compound	Assignment							
	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	$H(7)^{b}_{exo}$	$H(7)^{b}_{endo}$
(C_7H_8)$Fe(CO)_3$, 2	3.25	5.13-5.29		2.99	5.74	5.08	2.29	2.29
7-Ph_3Ge, 21c	3.70	4.50-4.76		3.07	5.69	5.33	-	2.94
3-Ph_3Ge, 39a	3.28	4.82	-	2.94	5.75	5.14	(2.40)	2.40
6-Ph_3Ge, 39b	3.28	5.15-5.30		3.01	6.10	-	(2.42)	2.42

[a] δ(ppm) relative to internal TMS, solvent CS_2.

[b] The resonances due to the exo and endo protons on C(7) are overlapping and the individual chemical shift values of these protons have not been determined for (C_7H_8)$Fe(CO)_3$ in CS_2. The resonances are better resolved in benzene.[106]

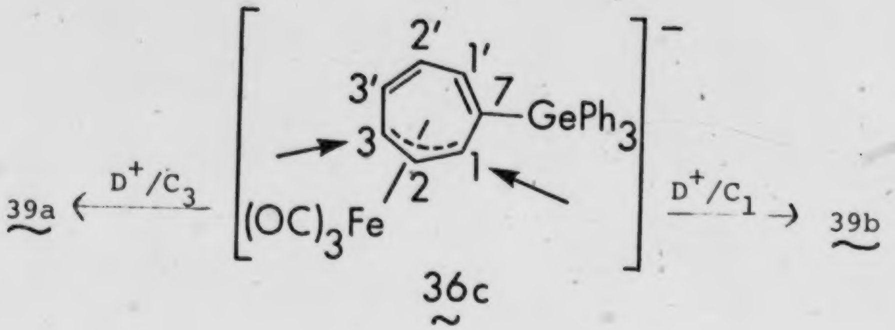
data and coupling constants do not allow the unambiguous assignment of the stereochemical position of the triphenylgermyl substituent in 21c. In addition the deuteration of 39a and 39b is only partial, 82 and 87% respectively, as determined by NMR spectroscopy. Since all 21c was consumed and the deuterium chloride was isotopically pure ($\geq$ 99%), the reason for partial deuteration is not well understood. It is possible that not all t-BuOH, formed in the synthesis of 36, was removed *in vacuo*. In that case, after redissolving 36 in THF, exchange could occur between t-BuOH and DCl, resulting in only partial deuteration of the *exo*-7-position. This then would further complicate the stereochemical assignment on the basis of the NMR spectral data. Maltz[105] and particularly Brookhart[106] demonstrated that selective *exo*-deuteration of 16 occurs and a similar stereochemistry seems plausible for 36. In the following Chapter the deuteration of the complexes 39 will be discussed and, reversing the argument by assuming that *exo*-deuteration of 39 occurs, these experiments will show that the *exo*-7-position is occupied predominantly by deuterium atoms. Deuteration of (C_7H_8)-$Fe(CO)_3$ is known to be stereoselective ($\geq$ 95%) and *exo*.[106]

d. Solution structure of $[(Ph_3GeC_7H_6)Fe(CO)_3]^-$.

The selective and exclusive formation of 39a and 39b upon deuteration of 36 is interesting. It also seems to require the presence of one predominant bonding form of 36 in solution instead of a random mixture of forms 36a-36h. It is furthermore interesting to note that by the application of an assumption derived from the recently formulated rules concerning nucleophilic addition to coordinated unsaturated hydrocarbon ligands in cationic organometallic complexes[115] a preponderant solution structure can be deduced which could lead to the formation of the 3-Ph_3Ge and 6-Ph_3Ge isomers exclusively.

The rationale behind the above rules focuses upon the relative amount of positive charge carried by the different carbon atoms of the coordinated unsaturated organic moieties. Particularly in the case of small and highly charged nucleophiles the rates of addition are charge rather than orbitally controlled.[169] Extending these observations to electrophilic attack by D^+ one would expect the regiospecificity to be governed by the *negative* charge on the particular carbon atoms, assuming that the electrophilic deuteration too is kinetically rather than thermodynamically controlled. For the η^3-coordinated cycloheptatrienyl ligand this means that attack by D^+ should preferentially occur at the terminal carbon atoms of the η^3-allyl part of the seven-membered ring. Returning now to the products observed in the reaction of 36 with D^+, we conclude that the dominant solution structure of 36 is best represented by 36c.

Scheme VIII.

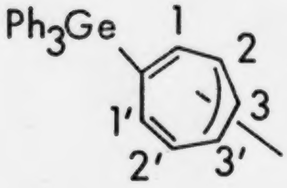


Scheme VIII. Deuteration of $[(Ph_3GeC_7H_6)Fe(CO)_3]^-$.

For 36c attack of D^+ at C(1) will yield 39b, the minor component, while attack at the sterically less crowded C(3) yields 39a, the major component. All other η^3- or η^4-bonding modes lead to a prediction which is different from the experimental results. A possible flaw in the above deduction could arise from the unusual distribution of the negative charge calculated to occur in the more symmetrical anion 16.[83] If this distribution holds in the present case it could be argued that the inner carbon atoms of the free diene moiety should be attacked in preference. However, with this view none of the possible isomers, or combinations thereof, lead to exclusive 3-Ph_3Ge and 6-Ph_3Ge isomer formation. Thus 36c and attack at the terminal allyl carbon atoms are tentatively preferred at the present time.

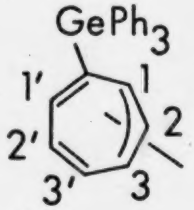
The postulated solution structure of 36 should be supported also by the relative chemical shift values of the protons 1 and 1', 2 and 2', and 3 and 3'. There are several factors which can influence the chemical shifts of the ring-protons in this anion. First of all, there is the empirical observation that the outer-allyl protons in neutral η^3-C_7H_7 complexes resonate at lower field than the central allyl proton, e.g. for $(C_7H_7)Fe(CO)_3SnPh_3$ the values are δ4.4 and δ3.4 ppm, respectively. Secondly, the outer diene protons in the uncoordinated diene moiety appear at lower field in the neutral η^3-C_7H_7 complexes than the inner diene protons. The reverse is true for a coordinated diene fragment in, for example, the dinuclear compounds prepared by Cotton and co-workers.[62c,64] The diene resonances in 22a occur at δ5.7 for H(4) and H(4'), and at δ6.4 ppm for H(3) and H(3'). Thirdly, the triphenylgermyl substituent appears to be able to exert a deshielding effect upon the neighboring protons. A fourth factor which can play a very important role in deciding the chemical shift values of the respective resonances in 36 is the presence of the negative charge. Regretably we know of no model compounds from which the magnitude of this effect could be calculated. Thus the application of the above criteria to justify 36c, or any other isomer, would be inappropriate. Realistically it must be admitted that, although the selective isomer formation upon deuteration bespeaks for the presence of one dominant isomer of 36 (possibly 36c) in solution, the unambiguous assignment of the ground state structure of 36 must await an X-ray structural determination or the observation of the ^{1}H low temperature limiting spectrum.

The above exercise is more justifiably applicable to compound 37 since we do not have to deal with the unknown effect of the negative charge. The four structural possibilities for this neutral compound and the predictions for the relative order of their chemical shift values are schematically shown below.



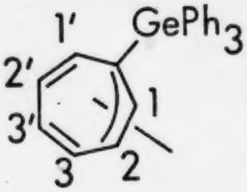
$\delta_{1,1'} > \delta_{2,2'} > \delta_{3,3'}$

37a



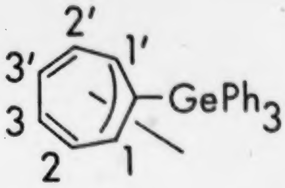
$\delta_{1,1'} \geq \delta_{3,3'} > \delta_{2,2'}$

37b



$\delta_{3,3'} > \delta_{2,2'} \simeq \delta_{1,1'}$

37c



$\delta_{2,2'} > \delta_{3,3'} > \delta_{1,1'}$

37d

The observed order of the chemical shift values is $\delta_{1,1'} > \delta_{2,2'} > \delta_{3,3'}$ and structure 37a is therefore assigned as the dominant species present in solution. It is also noted that, on the basis of the above arguments, the ground state solution structures of 36 and 37 are different. Again it is emphasized that these assignments are tentative, variable temperature ^{1}H and ^{13}C NMR studies are pursued in order to obtain further evidence with respect to the solution structure of the species 36 and 37.

Conclusions

The comples (*exo*-7-$Ph_3GeC_7H_7$)$Fe(CO)_3$ can be deprotonated, and it is concluded that *endo*-deprotonation occurs. In 21b, the Me_3Ge-substituent occupies the *exo*-7 position as determined by crystallographic analysis. The similarities of the physical properties, infrared, ^{1}H and ^{13}C NMR, and mass spectral characteristics of the complexes 21 indicate an identical stereochemical arrangement for 21a and 21c. Abstraction of the *endo*-proton of 21c thus occurs by the action of t-BuOK in tetrahydrofuran resulting in an air-sensitive red solution.

The anion $[(Ph_3GeC_7H_6)Fe(CO)_3]^-$ has been characterized by infrared and ^{1}H and ^{13}C NMR spectroscopic studies, and by its reactivity. The reactions of 36 with Me_3SiCl, Ph_3SnCl and particularly D^+ have been described. 36 can be titrated with DCl to form a 2:1 mixture of *exclusively* two geometrical isomers, $(3\text{-}Ph_3Ge,exo\text{-}7\text{-}DC_7H_6)Fe(CO)_3$, 39a, and $(6\text{-}Ph_3Ge,exo\text{-}7\text{-}DC_7H_6)Fe(CO)_3$, 39b. The end point of the titration is indicated by the distinct colour change from red (36) to yellow (the complexes 39). The formation of only the 3-Ph_3Ge and 6-Ph_3Ge isomers of $(C_7H_6DGePh_3)Fe(CO)_3$ leads to the postulate that the dominant species in solutions of 36 is the isomer 36c. As for anion 16, the solution structure of 36 appears to be best represented by the η^3-allyl bonding mode with an uncoordinated diene moiety also present in the seven-membered ring. The relative order of the chemical shifts could be used to assign, tentatively, the solution structure of the compound $(\eta^3\text{-}Ph_3GeC_7H_6)Fe(CO)_3SnPh_3$.

The 2:1 mixture of the isomeric complexes 39a and 39b could be separated into its constituent components by repeated fractional crystallization. This not only allowed the spectral characterization of the compounds 39 but also offered a pivot in the seven-membered ring which can be applied to determine the regioselectivity of the electrophilic attack on the coordinated neutral cycloheptatriene moiety. This will be discussed in Chapter V.

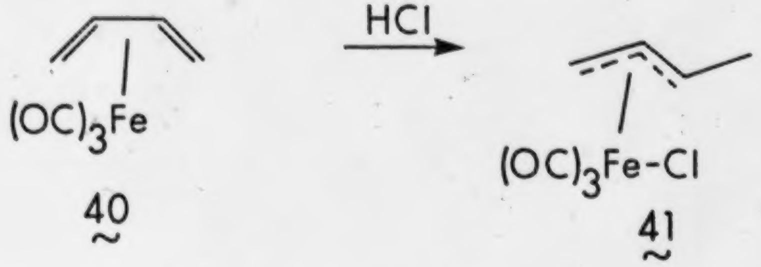
CHAPTER FIVE

REGIO- AND STEREOSELECTIVITY IN THE DEUTERATION OF THE 3-, 6-, AND 7-Ph_3Ge ISOMERS OF (η^4-$Ph_3GeC_7H_6R$)-$Fe(CO)_3$, R = H(7-Ph_3Ge) or D(3- and 6-Ph_3Ge).

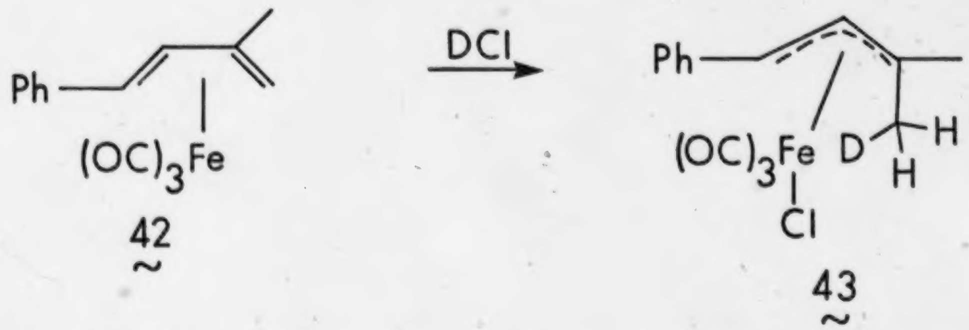
INTRODUCTION

The electrophilic addition to neutral organometallic complexes containing an unsaturated diene fragment has received considerable attention during the past ten years. Particularly the protonation reactions of diene tricarbonyliron complexes have been investigated.[106,170-173,175,177] The site of initial attack, the nature of the final products and the stereochemistry of the addition have all been studied and several explanations have been proposed to explain all the experimental observations. It now seems that some general patterns do govern the protonation reactions after all.

First, there is the nature of the final products and the site of attack. In organometallic compounds with a bound diene moiety, but with no uncomplexed double bonds present in the organic ligand, addition of H^+ occurs *endo* with respect to the metal center resulting in (η^3-allyl)iron species.[170,171,173] Depending on the coordinating ability of the counterion present, a coordinatively saturated, neutral (η^3-allyl)$Fe(CO)_3X$ (X = halide, for instance) complex can result, or, in the case of weakly coordinating anions like the trifluoroacetate ($CF_3CO_2^-$) or fluorosulfonate (FSO_3^-) anions, an η^1-η^3-allylhydridoiron species can be observed.[173] For example, (butadiene)tricarbonyliron[172] or (1-phenyl-3-methylbutadiene)tricarbonyliron[170,171] react with HCl or DCl to yield the (η^3-allyl)chlorotricarbonyliron complexes 41 and 43 respectively, equations (27) and (28).

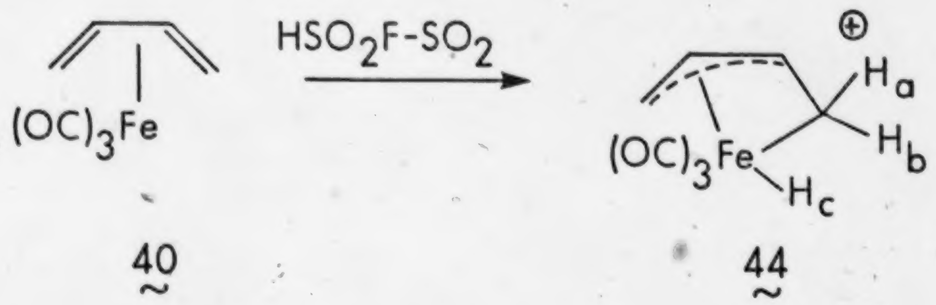

HCl
$(OC)_3Fe$
$(OC)_3Fe-Cl$
40
41

(27)


DCl
Ph
$(OC)_3Fe$
Ph
$(OC)_3Fe$
Cl
D
H
H
42
43

(28)

On the other hand the protonation of (butadiene)tricarbonyliron in HSO_3F-SO_2 or $CF_3COOH-HBF_4$ leads to the formation of the cationic (η^1-η^3-allyl)hydridotricarbonyliron species 44, equation (29).


HSO_2F-SO_2
$(OC)_3Fe$
⊕
H_a
H_b
$(OC)_3Fe$
H_c
40
44

(29)

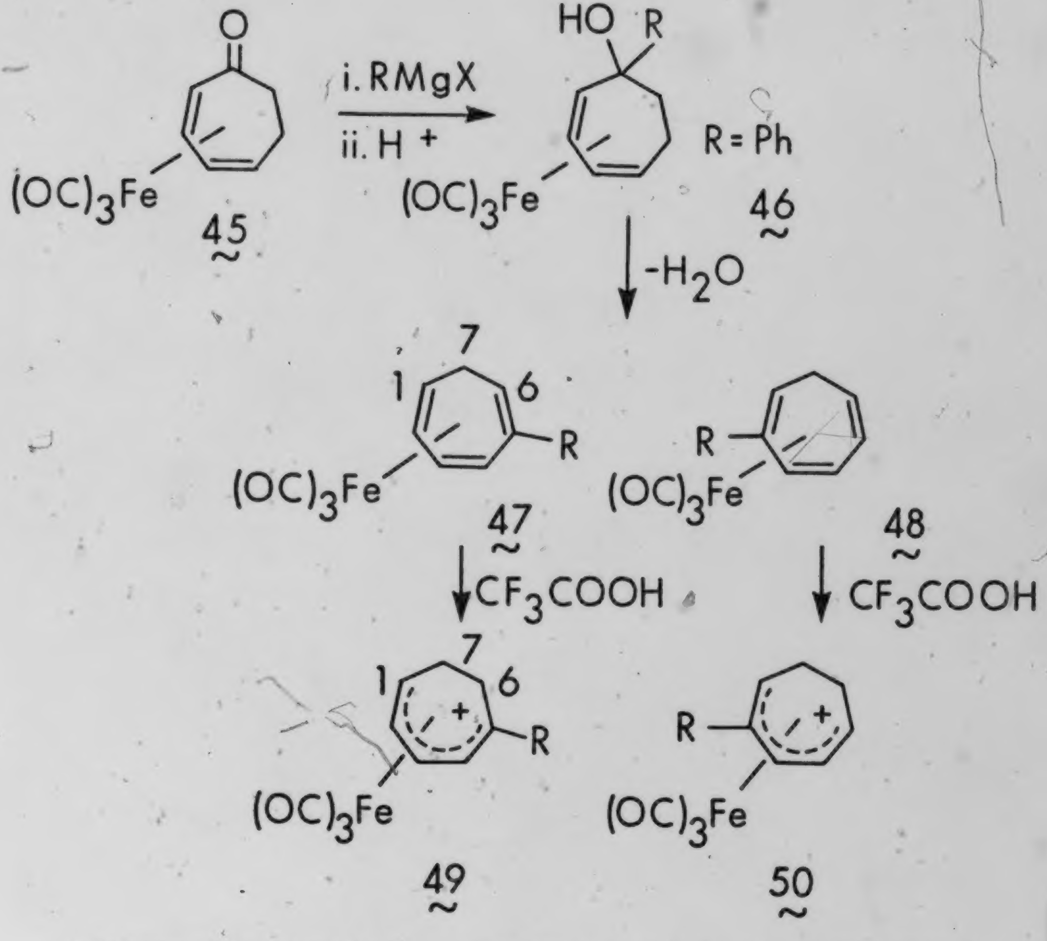
In the latter case no coordinatively unsaturated [(η^3-allyl)Fe(CO)$_3$]$^+$ species have been detected. If a neutral coordinatively saturated species would form initially, oxidative addition, i.e., insertion of iron into a C-H bond, might well occur simultaneously with the departure of the anionic ligand from the iron center and lead to the formation of 44. That weakly coordinating ligands, e.g. $CF_3CO_2^-$, can be covalently bound to the iron atom has been demonstrated.[173] However, it is worthwhile to observe that such a coordinatively unsaturated intermediate can help to explain the observed scrambling of the hydrogens, H_a, H_b, and H_c in 44.[173] In this regard the isolation and characterization of a distinctly unsaturated 16-electron species, [Fe(η^3-C_8H_{13})(P(OMe)$_3$)$_3$]$^+$, is of significance.[174] The formation of the latter species seems to occur *via* a hydrido intermediate resulting in the exclusive addition of H^+ (or D^+) *endo* to the metal therewith supporting the earlier contention of Whitesides that protonation of (cyclohexadiene)tricarbonyliron occurs *endo* to the iron center.[170,171,174]

The protonation of organometallic complexes which contain one or more uncomplexed double bond(s) in conjugation with a coordinated diene moiety is mechanistically different from the situation discussed above. Generally protonation is considered to occur at the outer carbon atom of the uncoordinated double bond.[178] It was however only very recently that McArdle and co-workers established indirectly that protonation of (cycloheptatriene)tricarbonyliron also follows this pattern and occurs selectively at C(6)*.[80] These workers obtained, from the reactions of the (cycloheptatriene)tricarbonyliron complex 45 with Grignard reagents followed by dehydration of the resulting alcohols, a mixture of the 2- and 5-substituted (cycloheptatriene)tricarbonyliron complexes 47 and 48, respectively,

---

*For the sake of consistency all carbon atoms in the above structures are numbered such as to give the outer carbon atom of the bound diene fragment, i.e. the carbon atom adjacent to the methylene bridge in 2, the number 1. This numbering system is retained in the protonated derivatives.

Scheme IX*.[80] From the ^{1}H NMR spectrum of the mixture a



O
i. RMgX
ii. H +
$(OC)_3Fe$
45
HO R
R = Ph
$(OC)_3Fe$
46
$-H_2O$
7
1
6
R
$(OC)_3Fe$
47
R
$(OC)_3Fe$
48
CF_3COOH
CF_3COOH
7
1
6
+
R
$(OC)_3Fe$
49
R
+
$(OC)_3Fe$
50

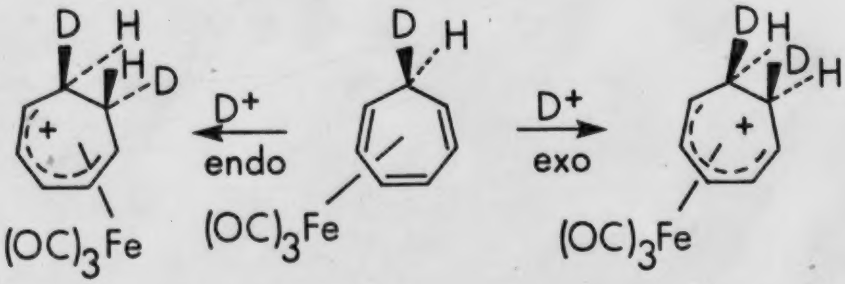
Scheme IX. Synthesis and protonation of substituted (cycloheptatriene)tricarbonyliron complexes.[80]

---

*We believe that the assignment by McArdle *et al.*[80] of the "characteristic ten-line multiplet" in the ^{1}H NMR spectrum of 2 to H(6) is incorrect. Selective decoupling experiments lead us and Brookhart[106] to assign this multiplet to H(5). Fortuitously this does not effect the final assignment of the structures above, even though the argumentation would be different. (The spectra of $(C_7H_8)Fe(CO)_3$ in various solvents are shown in Chapter VII).

1:1.6 ratio of 47 to 48 was determined. The protonation of this mixture of 47 and 48 with CF_3COOH in $CDCl_3$ resulted in the formation of the complexes 49 and 50 in exactly the same ratio. Attack at the uncoordinated double bond is therewith established.*

One question remains however. As *endo*-protonation occurs in dienetricarbonyliron complexes which do not contain additional free double bonds, will this also be the case in (η^4-cycloheptatriene)tricarbonyliron? An elegant study by Brookhart and co-workers clearly shows that in this complex *exo*-deuteration occurs.[106] These workers studied the electrophilic attack of D^+ on (exo-7-DC_7H_7)$Fe(CO)_3$, equation (30).



52 51 53

(30)

Compound 51 undergoes *exo*-D-addition as determined by the absence of a significant resonance at the *exo*-proton positions in the ^{1}H NMR spectrum of the dideuterated product. This result is in line with the limited data available on other polyenetricarbonyliron derivatives, e.g. for $(C_8H_8)Fe(CO)_3$.[178]

---

*If protonation would have occurred at C(1) of the coordinated double bond the same complexes would have resulted but in a different ratio, namely 0.6:1.

The fractional crystallization of a mixture of the complexes 39a and 39b resulted in the isolation of each of the two isomers as described in the Chapter IV. Thus three separate geometrical isomers of $(Ph_3GeC_7H_6R)Fe(CO)_3$, R = H or D, are available for further study. In this Chapter we report the results of the deuteration of each isomer. These reactions were undertaken in order to (i) establish the reactivity of the above complexes towards H^+ or D^+, (ii) to ascertain the regioselectivity* of the electrophilic attack, and (iii) to determine the stereochemistry of the deuteration of these substituted cycloheptatriene derivatives.

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*At this point a note regarding the definitions of selectivity and specificity seems warranted. If a reaction of a single isomer results in the formation of predominantly one structural isomer, the reaction is said to be *selective* as to structural isomer formation and one can speak of the degree of selectivity. If however a mixture of isomers is present as the starting material and each isomer yields - under identical reaction conditions - one particular, but different isomer as the product, then the reaction is said to be *specific*. A reaction which is 100% selective can be said to be specific as well.[176]

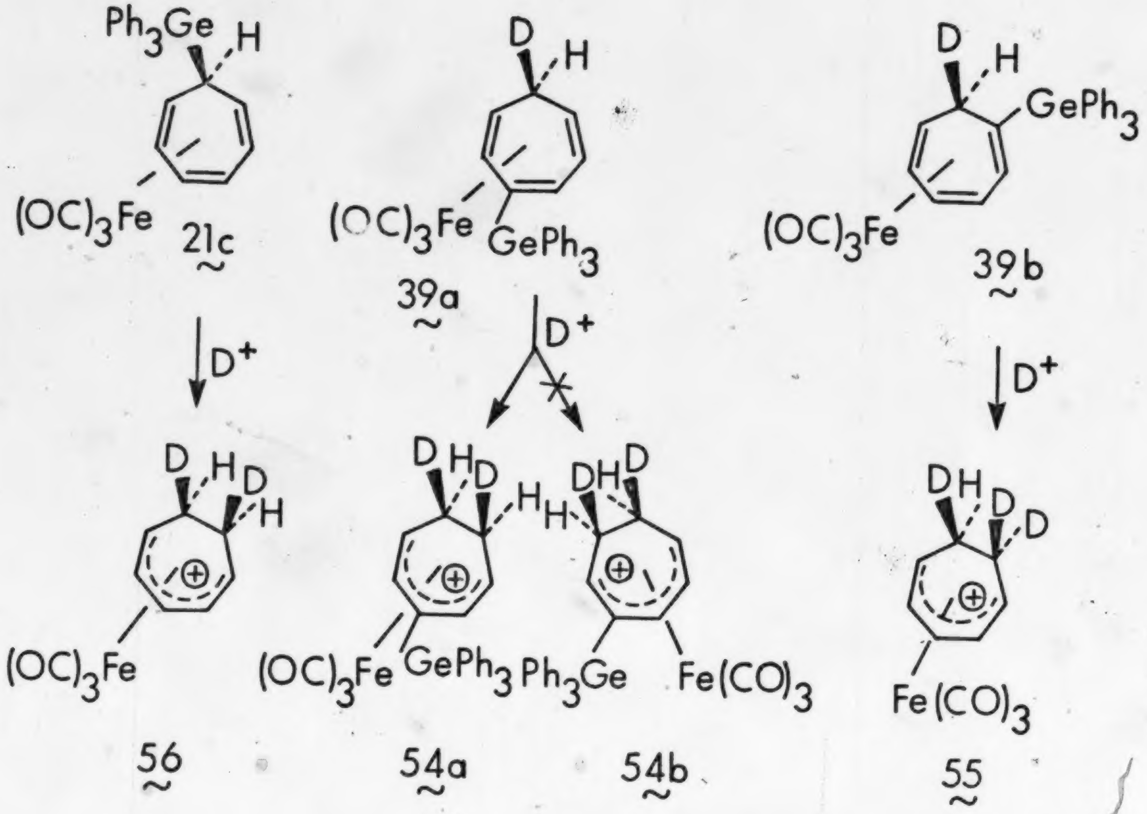
Results and Discussion

All reactions described in this Chapter were performed by adding, *via* a syringe, degassed deuterated trifluoroacetic acid, TFA-d_1 (~.25 ml), to a cooled (T ≤ -20°C) NMR tube, which was equipped with a serum stopper and contained 21c, 39a, or 39b (~50-75 mg), dissolved in degassed dichloromethane-d_2 (.3 ml) with a trace of TMS as internal reference. Under these conditions a large excess of TFA-d_1 is present. Deuteration of the 3-Ph_3Ge and 6-Ph_3Ge isomers of $(Ph_3GeC_7H_6D)Fe(CO)_3$ appears as a convenient route towards determining the regio- and stereoselectivity of the electrophilic attack. However, let us consider first the non-deuterated isomer 21c. It was anticipated that although the reaction of 21c would not allow us to elucidate the actual site of addition, C(1) or C(6), information regarding the stereochemistry might well become available. Particularly, if deuteration occurs *exo* in 21c two *endo*-hydrogens would result which might exhibit only a small chemical shift difference and, more significantly, should couple strongly (small dihedral angle) to the adjacent hydrogen atoms of the ring. The reverse would be true for *endo*-deuteration, i.e., a larger chemical shift difference between the 6-*exo* and 7-*endo* protons and a smaller coupling constant for the *exo*-hydrogen atom would be expected. The reaction of 21c with TFA-d_1 resulted in a pale yellow solution which exhibited signals in the ^1H (100) NMR spectrum at δ7.07 (1H), 5.93(2H), 4.90(2H), 2.66, and 1.86 (the last two resonances having a total intensity of 2H) ppm. These chemical shift values are, within experimental error, identical to those of $[(exo\text{-}6,7\text{-}C_7H_7D_2)Fe(CO)_3]^+$.[106,177] The reported values for the latter species, 53, are: δ7.11, 6.00, 4.98, and 2.69 ppm, but with only a small residual peak at δ1.87 ppm, the *exo*-hydrogen region in this type of complexes.[106] The intensity ratio of these peaks was also 1:2:2:2. Moreover, the coupling patterns observed in both instances are very similar in appearance. Thus the cationic species resulting from deuteration of 21c can readily be identified as $[(C_7H_7D_2)Fe(CO)_3]^+$, 56. It appears that under the experimental conditions cleavage of the germanium-carbon(sp^3) bond occurs. Initial attack of D^+ could occur either at C(1) (or C(6)) or at the germanium-carbon bond (C(7)). However, a decision regarding this aspect cannot be made on the basis of the data presently available. There is one other puzzling fact which cannot easily be explained. If one assumes that the deuteration at C(1) (or C(6)) occurs exclusively *exo*, as demonstrated by Brookhart *et al.* for 51,[106] then the remaining deuterium atom is distributed over both the *exo*- and *endo*-positions at carbon atom C(7), i.e. 30% *exo*-D and 70% *endo*-D. The total intensity of the *exo*- (70%) and *endo*- (30%) hydrogen atoms at C(7) is 1.0, and exactly two deuterium atoms are thus present in this cation.

This somewhat surprising result, even though the germanium-carbon bond is generally considered to be weaker than the carbon-carbon bond,[179] offsets any definite conclusion as to the stereochemistry of the electrophilic attack at C(6). The total intensity of the resonances at δ2.66 ppm, i.e. the *endo*-hydrogen positions, is larger than unity (1.3), a result which is consistent with the proposed *exo*-addition to the ring and the loss of stereochemistry occurring during C-Ge bond cleavage.

Although the above result was not very promising as to the course of the reactions of 39a and 39b with TFA-d_1, we nevertheless examined these reactions as well. The results are schematically represented in Scheme X and are tabulated in Table XX. All reactions were preformed at T ⩽ -20°C and the initial ^1H NMR spectra were recorded at -25°C. Subsequent warming of the solutions to ambient temperature did not change the appearance of the spectra.

As shown in Scheme X the addition of TFA-d_1 to 39a resulted in the synthesis of a symmetrical cation, 54a. Resonances for 54a were observed at δ5.73, 4.85, and 2.74 ppm while a residual resonance is seen at δ2.00 ppm. Particularly noteworthy is the absence of any signal at δ ~7.0 ppm, assignable to hydrogen H(3), indicating the presence of the triphenylgermyl substituent at carbon


Ph3Ge
H
(OC)3Fe
21c
D
H
(OC)3Fe
GePh3
39a
D
H
GePh3
(OC)3Fe
39b
D+
D+
D+
D
H
D
H
(OC)3Fe
56
D
H
D
H
(OC)3Fe
GePh3
54a
D
H
D
H
Ph3Ge
Fe(CO)3
54b
D
H
D
D
Fe(CO)3
55

Scheme X. Deuteration of three triphenylgermyl substituted (cycloheptatriene)tricarbonyliron derivatives.

TABLE XX

^{1}H NMR data for the deuteration reactions of the triphenylgermyl substituted cycloheptatrienetricarbonyliron derivatives.[a,b]

Reaction (product)	Assignment				
	H_1	$H_{2,2'}$	$H_{3,3'}$	$H_{4,4'}$[c]	
				exo	endo
21c + D^+ (**56**)	7.07	5.93	4.90	1.86	2.66
39a + D^+ (**54a**)	-	5.73	4.85	(2.00)	2.74
39b + D^+ (**55**)	7.09	5.97	4.93	(1.92)	2.78
51 + D^+ (**53**)[d]	7.11	6.00	4.98	(1.9)	2.69

---

[a] In $CF_3COOD/CD_2Cl_2/TMS$ (.25/.30/.05 ml).

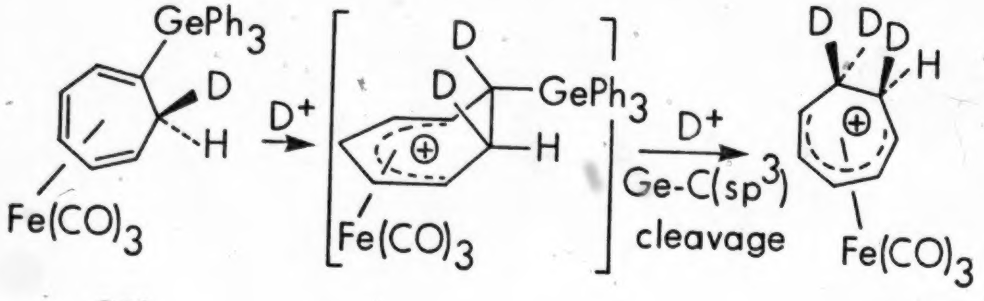
[b] Chemical shift values in δ ppm from internal TMS.

[c] The relative intensities of *endo* and *exo* hydrogen atoms are discussed in the text.

[d] From reference 106.

atom C(3). This in turn establishes the attack by D$^+$ at C(6), i.e. addition at the uncoordinated double bond occurs. The exclusive formation of 54a demonstrates the high regioselectivity of the electrophilic addition. It is evident that the germanium-carbon (sp^2) bond is more resistant towards electrophilic cleavage by D$^+$ than the Ge-C(sp^3) bond in 21c. The increased stability of the germanium-carbon(sp^2) bond with respect to the germanium-carbon(sp^3) bond was noted in Chapter II during the discussion of the mass spectral data of the complexes 21. Not only does the deuteration of 39a establish the regioselectivity of the attack, stereoselectivity is indicated as well. Only an unresolved residual resonance is observed at δ2.00 ppm. This resonance position is typical for the *exo*-hydrogen atoms in this class of compounds.[106] It is recognized that the starting complexes 39a and 39b both contain deuterium in the *exo* position for more than 80%. The presence of the residual signal is thus not unexpected even though its intensity (.7H) is surprising. The ratio between the phenyl resonances and the resonances due to H(1,1'), H(2,2'), and *endo*-H(4,4') (2.93) also indicates that cleavage of the C(sp^2)-Ge bond might occur, as a side reaction to the deuteration of 39a at C(6). However, no resonances attributable to species of type 56 could be detected. Although the instability of the Ge-C bond in 21c precludes the isolation of the anticipated, triphenylgermyl-containing, isomeric cations, the deuteration of 39a with CF_3COOD indicates that *exo* attack on the *uncoordinated* double bond occurs.

The result of the reaction of 39b with TFA-d_1 was similar to the interaction of 21c with the acid, as cleavage of the germanium-carbon bond was observed again. This was confirmed by the chemical shift values obtained for the resonances present in the ^1H NMR spectrum of the reaction product. The observation of the resonace at δ7.09 (1H) is indicative of an (η^5-cycloheptadienyl)tricarbonyliron cation. A residual resonance for the endo hydrogens was observed in this NMR spectrum as well. However, the ratio between the phenyl resonances and the resonances due to H(1,1'), H(2,2'), and H(3) (3.09) is still equal, within the error limits of the integration, to the calculated value (3.00). Thus it seems that the high intensity of the resonances at δ1.92 and 2.78 (total 2.5H) are due to an unknown impurity. In view of the more pronounced resistance of the germanium-carbon (sp^2) bond towards cleavage under these reaction conditions the pathway shown in Scheme XI is tentatively proposed to account for the formation of the cation 55. The proposed cleavage of the germanium-carbon(sp^3) bond in Scheme XI is compatible with initial attack at C(6).


GePh3
D
H
Fe(CO)3
D+
D
D
GePh3
H
Fe(CO)3
D+
Ge-C(sp3)
cleavage
D
D
D
H
Fe(CO)3

39b

55

Scheme XI. The reaction of (6-Ph_3Ge,7-DC_7H_6)$Fe(CO)_3$ with CF_3COOD.

Based upon the above data, and upon the results obtained by McArdle *et al.*[80] electrophilic addition of H^+ or D^+ occurs preferentially at the *outer carbon atom* of the *uncomplexed* double bond in (η^4-RC_7H_7)$Fe(CO)_3$ derivatives, and by analogy the parent molecule 2 most probably undergoes similar attack.

Conclusions

The deuteration of triphenylgermyl substituted (cycloheptatriene)tricarbonyliron derivatives appears to occur *regio*selective at C(6), the outer carbon atom of the uncoordinated double bond. Together with analogous results obtained by McArdle and co-workers[80] these data are readily construed as to be indicative of regioselective attack of H^+ or D^+ at C(6) in the unsubstituted parent molecule, $(C_7H_8)Fe(CO)_3$, as well. Thus a long standing controversy as to the actual site of electrophilic attack in this molecule seems to have been resolved.

Although the *stereo*selectivity of this addition had already been investigated[106] the present data support the earlier observations that *exo*-addition at C(6) takes place. The sensitivity of the germanium-carbon(sp^3) bond towards cleavage by trifluoroacetic acid under the reaction conditions employed unfortunately complicated the simple deuteration reactions looked for. It certainly is worthwhile to search for milder protonating agents in order to achieve, in particular, the synthesis of $[(endo\text{-}6\text{-}Ph_3GeC_7H_8)Fe(CO)_3]^+$. Subsequent *exo*-7-deprotonation of this species with, for example, a hindered base, could lead to the elusive $(endo\text{-}7\text{-}Ph_3GeC_7H_7)Fe(CO)_3$, the stereochemical counterpart of the complexes **21c**. On the other hand, the use of equimolar amounts of D^+ could also prevent the cleavage of the Ge-C bond and this is being investigated. We are presently isolating the cation 54a as its BF_4^- salt in order to complete the full characterization of this ion and to substantiate the preliminary results reported here. Deprotonation reactions of 54a with Lewis bases could lead to either the 3-Ph_3Ge or the 4-Ph_3Ge isomer of $(Ph_3GeC_7H_7D)Fe(CO)_3$.

CHAPTER SIX

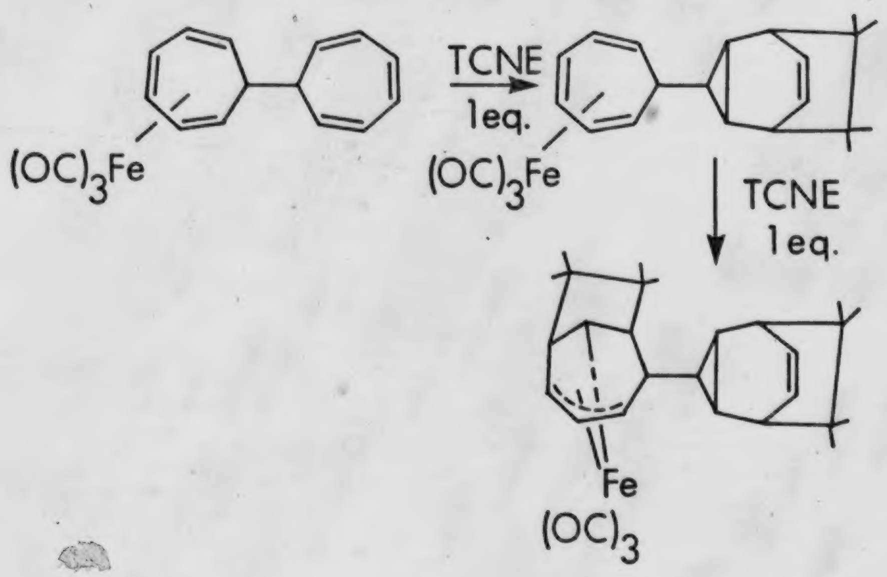
MISCELLANEOUS REACTIONS OF (*exo*-7-$Ph_3GeC_7H_7$)$Fe(CO)_3$ AND (η^3-C_7H_7)$Fe(CO)_3SnPh_3$.

INTRODUCTION

In Chapter II the synthesis of the compounds 21, (η^4-$R_3MC_7H_7$)$Fe(CO)_3$, MR_3 = $SiMe_3$, $GeMe_3$, and $GePh_3$, and 22, (η^3-C_7H_7)$Fe(CO)_3MPh_3$, M = Sn, Pb, was reported. These complexes exhibited characteristic stereochemically nonrigid behaviour. In Chapter IV the reaction of (η^4-$Ph_3GeC_7H_7$)$Fe(CO)_3$ with potassium t-butoxide was presented. This resulted in the *endo*-deprotonation of complex 21c, a stereochemical outcome which is different from all other known deprotonation reactions. The reactivity of complex 21c towards D^+ was investigated and described in Chapter V. In this Chapter some additional reactions of 21c and 22a are described. These reactions were initiated in order to explore the synthetic applicability of the new compounds.

The reactions of (C_7H_8)$Fe(CO)_3$ with several electrophilic and dienophilic reagents, e.g. phenylisocyanate[187,188] dimethylmaleate[187,188] tetracyanoethylene[78,79,80,180] diphenylacetylene,[187,188], and dimethylacetylenedicarboxylate,[187] have been studied. It appears that these reactions proceed either *via* the preliminary complexation of the olefinic or acetylenic dienophiles to iron followed by *endo* addition[187] or by direct *exo* attack[78,187,188] (e.g. phenylisocyanate, TCNE) onto the coordinated organic moiety. TCNE is known to react with $(C_7H_8)Fe(CO)_3$ to yield an addition product which exhibits an interesting (η^4-1,2,3,5) coordination mode.[78,79] The structure of this adduct is shown in Figure VI. Related azepine- and troponetricarbonyliron derivatives are known to undergo a similar 1,3-, 1,5-, or 1,6-addition.[78,180,182] In contrast free cycloheptatriene is known to react with TCNE by a 1,4 addition.[181]

The reactions of substituted cycloheptatrienetricarbonyliron derivatives with these dienophiles have only received limited attention. An interesting report has been communicated by McArdle.[79a] The addition of TCNE to (7-cycloheptatrienylcycloheptatriene)tricarbonyliron, a ditropyl derivative, occurs first to the uncomplexed ring *via* a 1,4-addition and then to the η^4-coordinated C_7H_7 moiety *via* an *exo*-1,3-addition, Scheme XII.



Scheme XII. The addition of TCNE to (7-cycloheptatrienyl-cycloheptatriene)tricarbonyliron.

The complexes 21 appear as convenient starting materials to investigate the reactions of substituted (cycloheptatriene)tricarbonyliron derivatives with TCNE. Here the reactivity of 21c towards TCNE will be described.

The complexes 21 can also be regarded as potential precursors of the organic compounds $C_7H_7MR_3$, MR_3 = $SiMe_3$, $GeMe_3$, and $GePh_3$. In view of the low yields obtained in the direct synthesis of these compounds by the treatment of $(C_7H_7^+)BF_4^-$ with $(Ph_3M^-)Li^+$ [35a] it seemed worthwhile to study the possible removal of the tricarbonyliron unit from the $C_7H_7MR_3$ moiety. Although different methods have been reported to achieve this, for example by the substitution of the organic moiety by a phosphine ligand, the action of ethanolic cupric chloride[191] or aqueous ceric ion solutions, the action of MnO_2,[210] or the use of trimethylamine oxide,[189,190] only two methods appear applicable due to the sensitivity of the $C_7H_7MR_3$ fragments towards aqueous or ethanolic solutions.[35a] The reactions of **21c** with a Lewis base, Ph_3P, and with trimethylamine oxide will be described. Me_3NO is a mild decarbonylating agent, often employed both in the synthesis of (diene)tricarbonyliron complexes[190] and in their degradation.[189,190]

One type of reaction was immediately envisaged for the complex $(\eta^3\text{-}C_7H_7)Fe(CO)_3SnPh_3$, namely the possibility of coordinating a second transition metal moiety to the uncomplexed diene moiety of the seven-membered ring. Such a synthesis has been realized by Cotton and Reich for $(\eta^3\text{-}C_7H_7)Mo(CO)_2(C_5H_5)$.[64] The synthesis of an analogous complex would be relevant with respect to the relationships that might exist between the structural and fluxional parameters of stereochemically nonrigid cycloheptatriene derivatives. The synthesis of $(OC)_3Fe(C_7H_7)Mo(CO)_2(C_5H_5)$, **11**, was accomplished by the photochemical reaction of $(C_7H_7)Mo(CO)_2(C_5H_5)$, **8**, with $Fe(CO)_5$ in diethyl ether.[64] A yield of 40% was obtained in this reaction. In contrast the thermal reaction of **8** with $Fe_2(CO)_9$, at 80°C, produced only 5% of the dinuclear complex **11**. It seemed worthwhile to attempt the preparation of an analogous derivative of 22a, i.e. $(OC)_3Fe(C_7H_7)Fe(CO)_3SnPh_3$, by a similar photochemical route. Other synthetic routes are also available. The utility of the (heterodiene)tricarbonyliron complexes (benzylideneacetone)tricarbonyliron, $(BDA)Fe(CO)_3$, and (3-penten-2-one)tricarbonyliron as tricarbonyliron transfer reagents is well documented.[66,198,199] Especially $(BDA)Fe(CO)_3$ has received wide application in the selective trapping of short-lived dienes.[198] The mechanism of the transfer of the $Fe(CO)_3$ moiety from $(BDA)Fe(CO)_3$ to conjugated dienes has been studied by Brookhart [66,199] and Howell.[200] Initial cleavage of the Fe—heterodiene, C=O bond in $(BDA)Fe(CO)_3$ occurs, which is followed by the η^2-coordination of the incoming diene. The subsequent reversible dissociation of BDA forms the first step towards the η^4-coordination of the diene. The transfer of the $Fe(CO)_3$ fragment is generally effected in refluxing benzene at ~60°C. In view of the stability of 22a under these conditions the use of $(BDA)Fe(CO)_3$ or (3-penten-2-one)$Fe(CO)_3$ appears as a logical alternative in order to effect the transfer of the $Fe(CO)_3$ moiety to the η^3-cycloheptatrienyl ring in 22a. In certain cases preference is to be given to (3-penten-2-one)$Fe(CO)_3$ as a transfer reagent because the liberated ligand 3-penten-2-one can readily be removed from the crude reaction mixture *in vacuo*, in contrast, the use of $(BDA)Fe(CO)_3$ often requires the chromatographic separation of benzylideneacetone and the desired reaction product.[198] The reactions of 22a with each of the above reagents will be described in this Chapter.

The photochemical reactions of $(\eta^3\text{-}C_7H_7)Fe(CO)_3SnPh_3$ with ^{13}CO and $P(OMe)_3$ will also be discussed together with a ^1H NMR study of the stability of 22a under prolonged thermal and photochemical conditions. The latter study was initiated in order to obtain possible evidence for the conversion of 22a into $(7\text{-}Ph_3SnC_7H_7)Fe(CO)_3$.

Results and Discussion

1. $(\eta^4\text{-}7\text{-}Ph_3GeC_7H_7)Fe(CO)_3$

a. Reaction with tetracyanoethylene.

The dropwise addition of a solution of TCNE in CH_2Cl_2 to a similar solution of $(7\text{-}Ph_3GeC_7H_7)Fe(CO)_3$ at ambient temperature resulted in a dark green, cloudy solution. The infrared spectrum of the solution showed, besides intense carbonyl stretching bands due to 21c, weaker ν_{CO} bands at 2070 and 2010 cm^{-1}. Removal of the solvent and subsequent workup, in hexane and in dichloromethane, led to the isolation of the starting materials only. The above reaction conditions are similar to those employed in the treatment of $(C_7H_8)Fe(CO)_3$ with TCNE, which resulted in the formation of a novel adduct (see Chapter I).[78a,79b] Various reaction times and different isolation procedures did not change this result. In hexane weak terminal carbonyl stretching bands are observed at 2072 and 2014 cm^{-1}, in addition to the ν_{CO} of 21c. These absorptions could be taken as indicative of the formation of a complex containing the (η^4-1,2,3,5) coordination mode, as similar bands have been reported for the $(C_7H_8)Fe(CO)_3$-TCNE adduct (at 2073(s) and 2011(s,br) cm^{-1} in $CHCl_3$).[79b] Our inability to isolate any compound in this reaction, together with the surprising green colour of the resulting solution, contrasts sharply with the precipitation of the pure yellow products observed during the reactions of $(C_7H_8)Fe(CO)_3$,[79b] (N- methoxycarbonyl-azepine)- and troponetricarbonyliron with TCNE.[180] It appears that a different explanation than adduct formation for the observations made in the reaction of 21c with TCNE is more appropriate. TCNE is known to form charge-transfer complexes with organometallic substrates.[183] For example, TCNE and ferrocene form a green charge transfer complex and infrared studies show that the observed spectrum is essentially a superposition of the spectra of TCNE and ferrocene.[184] It was shown by an X-ray diffraction study[185] that interaction occurs between the filled π-orbitals of one cyclopentadienyl ring in ferrocene and the empty π* orbitals of TCNE. The interaction of $(toluene)Cr(CO)_3$ with TCNE results in a green solution from which no complex could be isolated.[186] If this reaction was performed in benzene no ESR signals could be detected, implying the absence of an ionic product like $[(OC)_3Cr(toluene)^+, TCNE^-]$, in this solvent of low dielectric constant. In nitrobenzene an ESR signal is observed for this species.[186] The observations made for the interaction of 21c with TCNE fit the above pattern. A charge transfer complex was probably formed, as indicated by the green colour of the solution, but upon crystallization only the starting materials were recovered, showing the reversible nature of the complex formation. The greatly decreased reactivity of 21c compared to $(C_7H_8)Fe(CO)_3$ is, at first sight, surprising. The electrophilic attack of TCNE on the latter complex has been shown to occur *exo* at C(6).[79b,180] Attack at this position in 21c is however severely hindered by the presence of the sterically demanding *exo*-7-triphenylgermyl group. 1,3-addition at C(6) thus becomes impeded and, instead, a charge transfer complex appears to be formed. Electronic factors may play an important role as well. That electronic factors can exert a determining influence upon the site of attack is shown in the reactions of TCNE with substituted (cyclooctatetraene)tricarbonyliron complexes.[195]

b. Reaction with Me_3NO. Discussion of the synthesis and properties of oxobis(triphenylgermanium).

As mentioned in the introduction to this Chapter trimethylamine oxide is considered to be a mild decarbonylating agent. The treatment of **21c** with a ∼15-fold excess* of Me_3NO, first at ambient temperature and later at ∼60°C in tetrahydrofuran resulted in a brown reaction mixture. Infrared spectra showed the absence of any carbonyl stretching frequencies indicating that complete decarbonylation and, by inference, complete disengagement of the organic moiety from the iron center had occurred. Extraction of the crude reaction product with hexane followed by crystallization gave oxobis(triphenylgermanium), $Ph_3GeOGePh_3$, identified by NMR and by mass spectrometry. The mass spectra data of $Ph_3GeOGePh_3$ are summarized in Table XXI. This compound was also encountered as a byproduct in the synthesis of **21c** (Chapter II). As noted, it was particularly difficult to separate $Ph_3GeOGePh_3$ from **21c**, repeated fractional crystallization being the only technique by which the two compounds could be separated. The absence of small amounts of $Ph_3GeOGePh_3$ in **21c** is best determined by mass spectrometry as ^1H NMR becomes less practical in indicating the presence of $Ph_3GeOGePh_3$ as the ratio $Ph_3GeOGePh_3$/**21c** decreases. The mass spectra of both compounds are shown in Figure XXXVI.

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[*] A large excess of Me_3NO with respect to the (diene)tricarbonyliron complex is required in order to achieve complete decarbonylation.[189,190]

TABLE XXI

Mass spectral data of oxobis(triphenylgermanium).[a]

Assignment	m/e	rel. abundance (%)
$Ph_3GeOGePh_3^+$	624	12.7
$Ph_3GeOGePh_2^+$	547	79.5
$Ph_3Ge_2O(C_6H_4)^+$	469	26.6
$Ph_3Ge_2O^+$	393	6.7
$Ph_3Ge(C_6H_4)^+$	381	6.4
Ph_3Ge^+	305	100.0
$C_7H_5Ge_2^+$	235	14.9
$PhGe(C_6H_4)^+$	227	21.3
$PhGe^+$	151	39.3
Ph^+	77	20.6
Ge^+	74	1.7

[a] 70 eV, 150°C. The most intense m/e-value within each cluster is given.

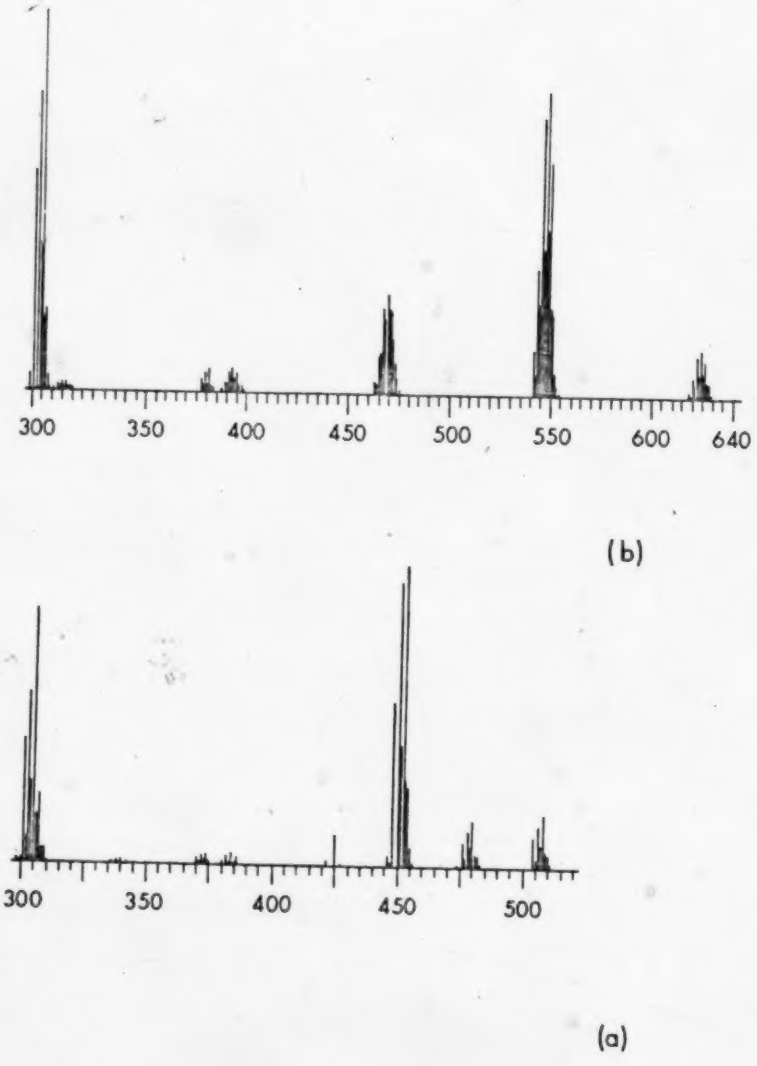

Figure XXXVI. Mass spectra of a $[7-(C_6H_5)_3GeC_7H_7]Fe(CO)_3$, and b $(C_6H_5)_3GeOGe(C_6H_5)_3$ (m/e-values $\geq$ 300).

It thus appears that the reaction of 21c with Me_3NO not only results in decomplexation of the substituted cycloheptatriene ligand but cleavage of the cycloheptatrienyl-$GePh_3$ bond occurs as well. The limited stability of this bond was also reflected in the mass spectral data of the complexes 21 and in the treatment of 21c and 39b with CF_3COOD (Chapters II and V). In the presence of the relatively strong nucleophilic agent Me_3NO, cleavage of the Ge-C(sp^3) bond occurs, possibly leading to $C_7H_7^+$, Me_3N and Ph_3GeO^-, in analogy to the action of Me_3NO upon coordinated carbon monoxide ligands.[189] The latter species could react with a second $(Ph_3GeC_7H_7)Fe(CO)_3$ or $(Ph_3GeC_7H_7)$ molecule to give $Ph_3GeOGePh_3$. The nature of the mechanism which gives rise to $Ph_3GeOGePh_3$ has however not been investigated. The electrophile Ph_3SiCl is known for its anomalous behaviour towards transition metal anions[111] (see Chapter II) and often the related species $Ph_3SiOSiPh_3$ is observed. No mechanism for its formation has been proposed.[111] Although the oxygen atom in the present case could well arise from the amine oxide,* this is not true for the reactions of R_3GeX with metal carbonylates.[193] For example, the treatment of $Na_2Fe(CO)_4$ with $2Me_3GeCl$ leads to trace amounts of

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*The formation of $Ph_3GeOGePh_3$ in the reaction of Ph_3GeBr with 16 might be due to the presence of residual t-BuOH formed in the deprotonation of $(C_7H_8)Fe(CO)_3$.

$Me_3GeOGeMe_3$, together with the desired complex $(Me_3Ge)_2Fe(CO)_4$.[193] The latter compound decomposes, both in the presence of oxygen and *in vacuo*, to give $Me_3GeOGeMe_3$. The oxygen atom in oxobis(trimethylgermanium) thus appears to arise through degradation of the iron carbonyl moiety in $(Me_3Ge)_2Fe(CO)_4$. A related example is found in the conversion of $(Ph_2Ge)_2Fe_2(CO)_7$ to $[(Ph_2Ge)_2O]Fe_2(CO)_8$.[194] The origin of the oxygen atom in $Ph_3GeOGePh_3$* thus remains obscure and could arise through either inter- or intramolecular decomposition. As $\underset{\sim}{21c}$ and $(Ph_3GeC_7H_7)$[35a] are stable at these reaction temperatures in the absence of Me_3NO, direct attack by the latter reagent on the $Ge\text{-}C(sp^3)$ bond appears as the most probable explanation for the formation of $Ph_3GeOGePh_3$.

c. Reaction with triphenylphosphine.

Two equivalents of triphenylphosphine and one equivalent of $\underset{\sim}{21c}$ were dissolved in toluene at ambient temperature and allowed to react. The reaction could be followed conveniently by monitoring the infrared spectra. No substitution occurred. Heating at ~73° for 48 h also did not lead to any changes in the infrared spectrum. Only upon refluxing the solution at 115°C for more than 72 h do the spectra indicate the formation of $(Ph_3P)_2Fe(CO)_3$, although the carbonyl stretching frequencies of **21c** are still dominant. $(Ph_3P)_2Fe(CO)_3$ was identified by comparing the position of the infrared absorption with the reported value.[197] Substitution of $(Ph_3GeC_7H_7)$ by Ph_3P thus occurs only at temperatures where thermal decomposition of **21c** is known to happen. This illustrates the stability of **21c** towards the substitution of the organic fragment by Lewis bases, and prevents a simple route towards $Ph_3GeC_7H_7$.

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*The crystal and molecular structure of $Ph_3GeOGePh_3$ has very recently been reported.[192]

2. $(\eta^3\text{-}C_7H_7)Fe(CO)_3SnPh_3$.

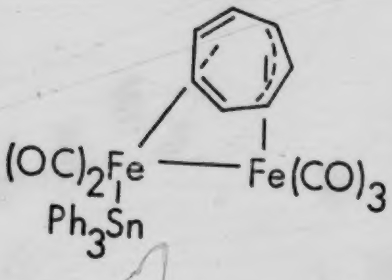
a. Reaction with $Fe(CO)_5$.

The irradiation of a mixture of **22a** and a large excess of pentacarbonyliron in diethyl ether in a photolysis vessel resulted in a deep red solution. After filtration to remove $Fe_2(CO)_9$ and removal of diethyl ether and excess $Fe(CO)_5$ *in vacuo*, the residue was extracted with toluene. Carbonyl stretching frequencies in toluene were observed at 2087.0(w), 2071.5(s), 2045.0(vs), 2011.5(s), 1990.0(m), and 1978.0(m) cm^{-1}, no bands due to **22a** were present at this stage. Crystallization of this solution was attempted but no crystalline or solid material would form. Further attempts to induce crystallization by e.g. the addition of hydrocarbon solvents also met with failure. Because the starting compound **22a** is unstable under most chromatographic conditions, particularly on alumina(II) and florisil, and as a similar stability of the desired product is to be expected, only chromatographic separations on silica gel were endeavoured. However, besides (C_7H_8)-$Fe(CO)_3$ no other compounds could be isolated or identified after chromatography. It was then decided to attempt the synthesis of $(OC)_3Fe(C_7H_7)Fe(CO)_3SnPh_3$ by use of the tricarbonyliron transfer reagents.

b. Reaction with $(BDA)Fe(CO)_3$.

Compound 22a was treated with $(BDA)Fe(CO)_3$ in benzene at ~60°C for 90 h. The reaction was followed by monitoring the decrease in the intensity of the ν_{CO} of the starting compounds and the appearance of new carbonyl stretching bands. Removal of benzene followed by the addition of hexane to the crude product gave a red solution from which a red solid slowly precipitated. This solution exhibited CO stretching maxima at 2046(m), 1992(m), 1983(s), 1954(m), and 1944(w) cm^{-1}. For the solid, mass spectrometry showed the presence of a cluster centered at m/e 694 which underwent the consecutive loss of at least five carbonyl ligands. ^1H NMR spectra of this powder, recorded in toluene-d_8, indicated the presence of more than one compound. A single sharp resonance was observed at δ 3.17 ppm, consistent with the presence of a fluxional C_7H_7 ring, which only started to broaden below -90°C. ^{13}C NMR spectra suggested the presence of just two compounds, one fluxional species exhibiting a sharp C_7H_7 resonance at δ 65.8 ppm, which broadened at lower temperatures but has not completely collapsed into the baseline at -125°C, and a second complex containing a static seven-membered ring at ambient temperature. Besides the resonances due to the phenyl groups, ^{13}C NMR signals were observed at δ32.9, 69.6, 75.7, 81.9, 89.6 and 103.7 ppm. The position of the latter resonances is typical of the ^{13}C resonances of the complexes of the type $(\eta^4\text{-}R_3MC_7H_7)Fe(CO)_3$.

Attempts to recrystallize this product in toluene-pentane solvent mixtures resulted only in the isolation of a very small amount of a brown-red powder. Carbon and hydrogen elemental analyses of this solid are in excellent agreement with the formulation of the obtained product as $(C_7H_7)Fe_2SnPh_3(CO)_y$, y = 5 or 6. In the absence of oxygen analysis a decision between a penta or hexacarbonyl species cannot be reached. Although no sufficient amounts of each of the compounds present in the above mixture could be obtained, the available data allow a tentative identification of one of the components. As noted, the elemental analyses are consistent with the formulation of one species as $(C_7H_7)Fe_2(CO)_{5\text{ or }6}SnPh_3$. The sharp ^1H and ^{13}C NMR signals observed for the cycloheptatrienyl hydrogen and carbon atoms point towards the presence of a cis-dinuclear cycloheptatrienyl complex containing a metal-metal bond. This class of compounds is known to exhibit sharp resonances for the hydrogen and carbon atoms of the cycloheptatrienyl ligand down to the lowest accessible temperatures.[112] The position of the resonances for the hydrogen and carbon atoms of the ring is also typical for this type of complex and shows the familiar upfield shift of these resonances compared to the mononuclear fluxional C_7H_7 complexes, due to the coordination of a second transition metal. The present complex is thus formulated as $(OC)_3Fe(C_7H_7)Fe(CO)_2SnPh_3$, $\underset{\sim}{57}$. There are



$\underset{\sim}{57}$

two other lines of evidence which support the above assignment. The mass spectrum of the above mixture shows the presence of clusters at m/e-values corresponding to the ions $(C_7H_7)Fe_2(SnPh_3)(CO)^+_{5-x}$, x = 0,1,2,3,4, and 5. Moreover the observed intensity ratios within each of these clusters agree well with the calculated intensity ratios. The extraction of further information from the mass spectra is precluded by the presence of the second complex. Secondly the anion $[(C_7H_7)Fe(CO)_3]^-$ reacts with transition metal electrophiles, $[Rh(CO)_2Cl]_2$, $[Re(CO)_3Br(THF)]_2$, and $[Mn(CO)_4Br]_2$, to yield *cis*-dinuclear heterometallic complexes.[112] Even if the second transition metal complex is "prepared to accept just three electrons from the anion", as in the case of $[Mn(CO)_4Br]_2$, which could lead to either a trans or a cis disposition of the transition metal moieties with respect to the C_7H_7 ring an alternative reaction occurs involving the additional elimination of a carbonyl ligand.[112] A similar reaction route can be envisaged for the formation of $(OC)_3Fe(C_7H_7)Fe(CO)_2SnPh_3$. This is supported by the ease of the dissociation of a carbonyl ligand from **22a**, *vide infra*. Both iron atoms in **57** achieve the 18-electron configuration by the formation of a Fe-Fe metal-metal bond. The composition of the second compound present in the obtained mixture remains obscure even though one is tempted to speculate. Based upon the typical ^{13}C NMR pattern observed at ambient temperature the presence of $(\eta^4\text{-}Ph_3SnC_7H_7)Fe(CO)_3$ would seem to be possible.

c. Reaction with (3-penten-2-one)$Fe(CO)_3$.

Realizing the inapplicability of chromatographic separation techniques for derivatives of **22a**, the above reaction was also carried out with (3-penten-2-one)$Fe(CO)_3$ as the tricarbonyliron transfer reagent with the hope of simplifying the isolation procedure. The reaction conditions were identical to the treatment of 22a with (BDA)Fe$(CO)_3$. However upon the addition of hexane to the red oil obtained upon the removal of benzene from the crude reaction mixture, a yellow solid formed. After extracting this solid with pentane the ambient temperature ^{1}H NMR spectrum of the residue in carbon disulfide showed the presence of a sharp resonance at δ5.11, assigned to 22a and another sharp resonance at δ3.66 ppm, in the intensity ratio 3:1. There also seemed to be a third, fluxional, species hidden in the baseline at this temperature (*vide infra*). Upon recrystallization of this yellow powder from dichloromethane *red* crystals were obtained which were subsequently identified by elemental analysis, infrared, and variable temperature ^{1}H NMR spectroscopy and by mass spectrometry as $(\eta^5\text{-}C_7H_7)Fe(CO)_2\text{-}SnPh_3$, 58. The physical properties and the stereochemically nonrigid behaviour of this η^5-cycloheptatrienyl complex are discussed in the following section. The resonance at δ3.66 ppm which was observed in the crude reaction mixture is again assigned to the dinuclear species 57. Realizing the different solvent systems employed, the difference in the chemical shift values of the C_7H_7 protons of 57 in the above two experiments becomes plausible. So far the separation of 22a and 57 proved to be impossible due to the very similar solubility characteristics of these two compounds.

Evidently the synthesis of trans-$(OC)_3Fe(C_7H_7)Fe(CO)_3$-$SnPh_3$ is not as straightforward as anticipated from the analogous transformation achieved by Cotton and Reich[64] for complex 8. In contrast at least two different fluxional and indubitably interesting complexes have been isolated, 58, and another complex which tentatively has been identified as 57.

d. Physical properties and stereochemical nonrigidity of $(\eta^5$-$C_7H_7)Fe(CO)_2SnPh_3$.

The synthesis of $(\eta^5$-$C_7H_7)Fe(CO)_2SnPh_3$, 58, has been described in the previous section (equation 31). The

$$22a \longrightarrow 58 + \mathrm{CO} \qquad (31)$$

compound was obtained as one of the products in the reaction of 22a with (3-penten-2-one)$Fe(CO)_3$. Here the infrared, mass and variable temperature ^1H NMR spectra of 58 will be described and discussed.

Infrared spectral data.

In dichloromethane 58 exhibits two terminal carbonyl stretching frequencies at 1994 and 1940 cm^{-1}, indicating the presence of two carbon monoxide ligands. The shift to lower frequency of the absorption maxima of 58 compared to 22a (2038.5, 1987.0, and 1957.5 cm^{-1}) are indicative of the increased π-backbonding to the remaining carbonyl ligands. Both the removal of one carbonyl group and the increased coordination of the cycloheptatrienyl ring to the iron center probably contribute to this effect.

Mass spectral data.

The mass spectral data of 58 are summarized in Table XXII. The decomposition pathways observed are typical for organometallic complexes. The loss of carbonyl ligands is a dominant process. The molecular ion, P^+, is not observed, but clusters assignable to $(P-CO)^+$ and $(P-2CO)^+$ are present. One of the major subsequent fragmentation pathways is formed by the cleavage of the Fe-Sn bond resulting in the species $C_7H_7Fe^+$, m/e 147, and Ph_3Sn^+, m/e 351. The characteristic breakdown patterns of the latter ions dominate the mass spectrum at lower m/e-values. The observed intensity ratios within the tin containing clusters agree well with those calculated. Important is the presence of the ions $FeSn^+$, $FeSn(C_6H_4)^+$, and $FeSnPh_2^+$, which support the existence of a direct iron-tin bond.

Variable temperature ^1H NMR spectral data.

The variable temperature ^1H NMR spectra of 58 in the range +80 to -70°C are shown in Figures XXXVII and XXXVIII. At $T \cong 40°C$ one single broad peak is observed for the protons of the cycloheptatrienyl ring. This resonance sharpens at higher temperatures until at $T > +80°C$ a sharp peak results at $\delta 4.51$ ppm. This behaviour is of course typical of a fluxional cycloheptatrienyl ligand. The

TABLE XXII

Mass spectral data of $(\eta^5\text{-}C_7H_7)Fe(CO)_2SnPh_3$.[a]

Assignment	m/e	rel. abund. (%)
$(C_7H_7)Fe(CO)SnPh_3^+$	526	4.0
$(C_7H_7)FeSnPh_3^+$	498	29.8
$SnPh_3^+$	351	37.3
$FeSnPh_2^+$	330	9.4
$SnPh_2^+$	274	16.0
$FeSn(C_6H_4)^+$	252	6.3
$(C_7H_7)(C_6H_5)Fe^+$	224	76.0
$SnPh^+$	197	47.3
$FeSn^+$	176	8.0
$(C_6H_5)_2^+$	154	34.6
$C_7H_7Fe^+$	147	43.8
$C_7H_6Fe^+$	146	64.5
Sn^+	120	37.0
$C_7H_7^+$	91	100.0

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[a] T = 165°C. Not corrected for ^{13}C.

[b] The m/e-value of all tin-containing ions corresponds to the ^{120}Sn-isotope.

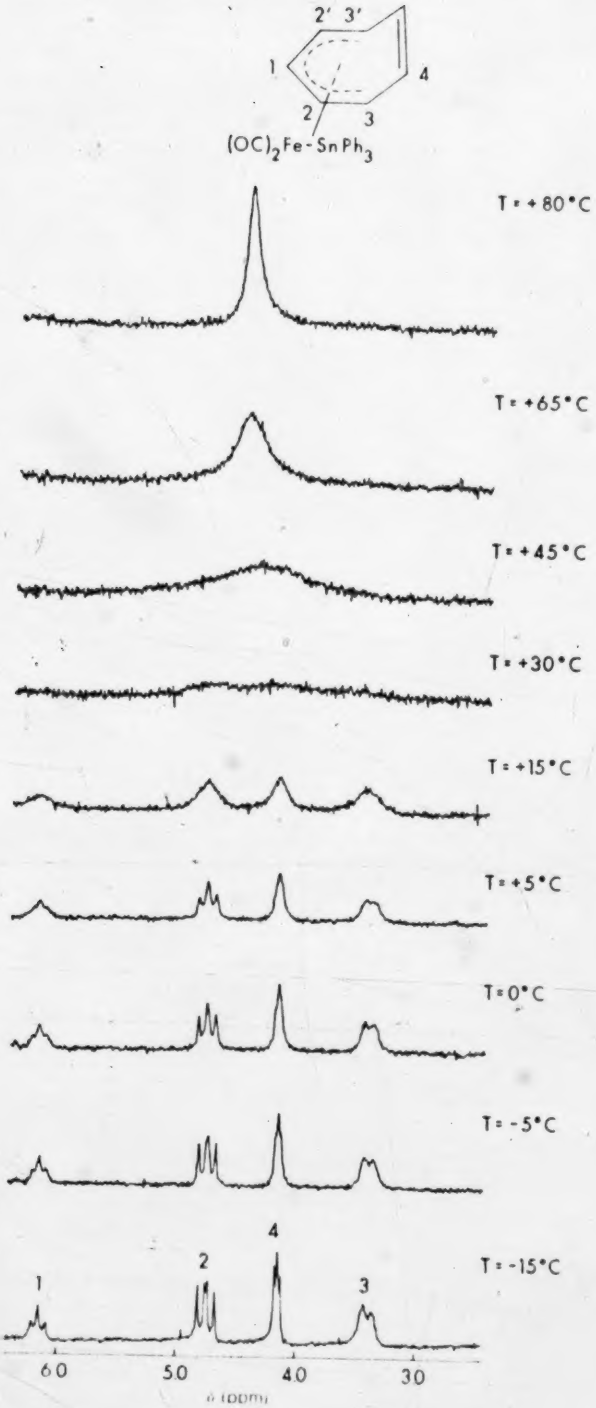


Figure XXXVII. Variable Temperature ^1H NMR Spectra of $(\eta^5-C_7H_7)Fe(CO)_2Sn(C_6H_5)_3$, +80°C to -15°C in toluene-d_8.

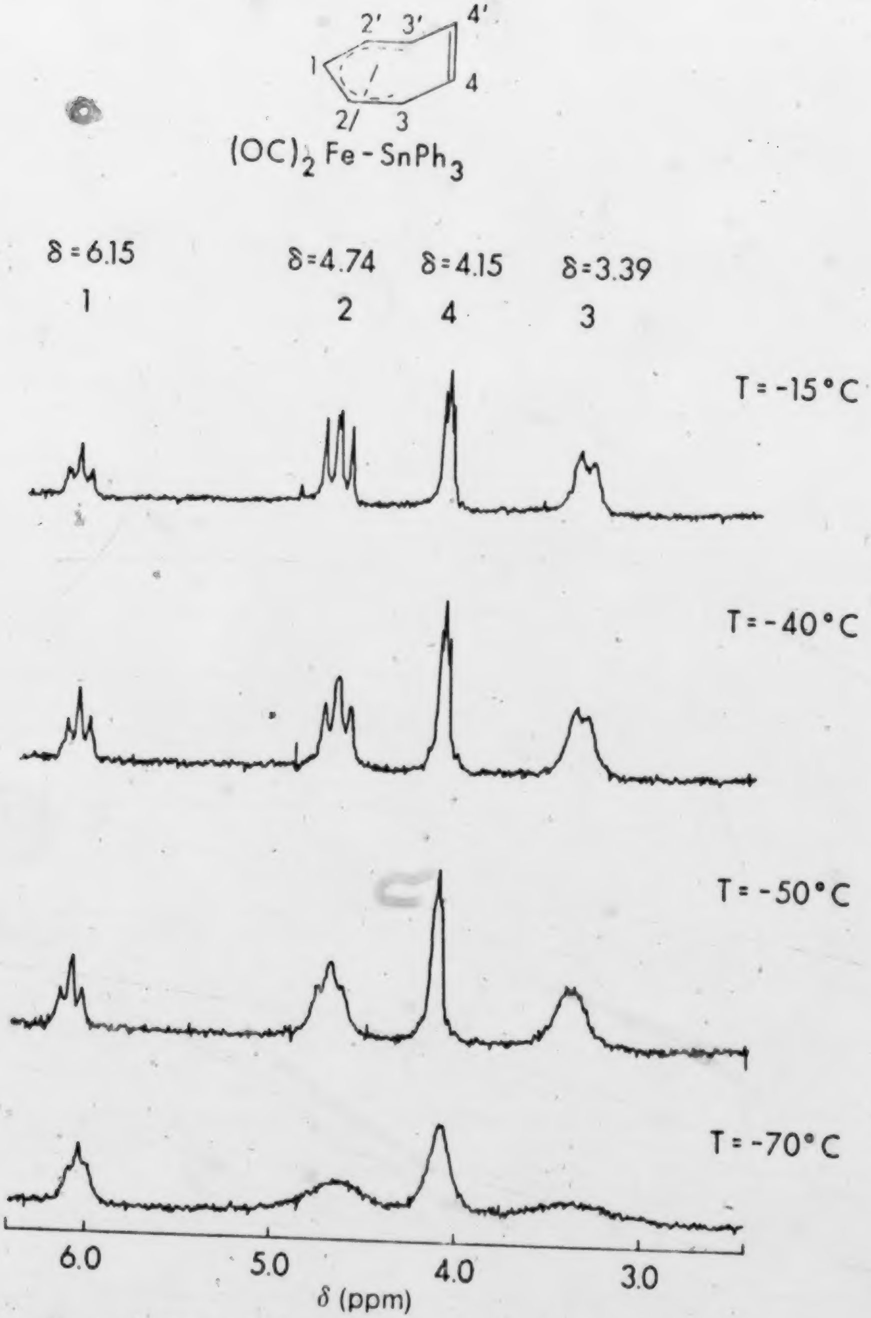


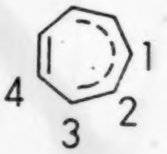
Figure XXXVIII. Variable Temperature ^{1}H NMR Spectra of $(\eta^5\text{-}C_7H_7)Fe(CO)_2Sn(C_6H_5)_3$. -15°C to -70°C in toluene-d_8.

limiting spectrum, with respect to the migration of the $Fe(CO)_2SnPh_3$ fragment about the C_7H_7 ring, is observed at T $\simeq$ +15°C. Four distinct resonances are now apparent at δ3.39, 4.15, 4.74, and 6.15 ppm. It is interesting to note the values of the coupling constants, $J_{1,2} \simeq 6.0$ Hz, $J_{2,3} \simeq 7.0$ Hz, and $J_{3,4} \simeq J_{3,4'} \simeq 3.0$ Hz. Other coupling constants are $\leqslant$ 1.0 Hz. The small value of the coupling constant between H(3,3') and H(4,4') is emphasized, as this points towards a rather large dihedral angle between these protons. This in turn indicates that the uncomplexed double bond in 58 is substantially bent away from the iron center. The linewidths of the resonances due to the protons 3,3' are rather large and are not resolved as well as the resonances due to the remaining protons. The possible significance of this is discussed below. The above data are tabulated in Table XXIII, and all assignments were confirmed by double irradiation experiments. Similar observations have been made for the complex $(\eta^5\text{-}C_7H_7)Mn(CO)_3$,[37], 59. Moreover both the relative chemical shift values and the magnitudes of the coupling constants are very similar to those observed for the manganese complex.[37] The lower chemical shift values observed for $[(\eta^5\text{-}C_7H_7)Fe(CO)_3]^+$ compared to 58 and 59, see Table XXIII, are not surprising in view of the positive charge carried by the latter species. It is noted that this shift has been associated with the aromatic character

TABLE XXIII

^{1}H NMR spectral data for η^5-cycloheptatrienyl complexes of the transition metals.[a]

Compound		Solvent	Assignment 1	2	3	4	Temp °C	$\delta(C_7H_7)$ at fast exchange obs.	calc.
$(\eta^5\text{-}C_7H_7)Fe(CO)_2SnPh_3$,[b]	**58**	toluene-d_8	6.15	4.74	3.39	4.15	-15°	4.51[f]	4.39
$(\eta^5\text{-}C_7H_7)Mn(CO)_3$[c]	**59**	acetone-d_6	7.10	5.42	3.53	4.70	-47°	4.85	4.91
$[(\eta^5\text{-}C_7H_7)Fe(CO)_3]^+$ [c]	**15**	acetone-d_6	8.48	6.70	5.13	5.48	-80°	6.10	6.16
$(\eta^5\text{-}C_7H_7)Fe(\eta^5\text{-}C_7H_9)$[d]	**13**	toluene-d_8	3.9 - 4.5		3.2	5.0	-10°	4.4	d
$(\eta^5\text{-}C_7H_7)Ru(\eta^5\text{-}C_7H_9)$[e]	**14**	benzene-d_6	3.9 - 4.3		3.0	4.6	e	e	e



[a] In δ(ppm) by appropriate conversion from internal solvent references.

[b] The phenyl protons were observed in the region δ6.90-7.93 ppm.

[c] See reference 37.

[d] No unambiguous assignments of many of the resonances could be made due to the complicated spectrum obtained.[81]

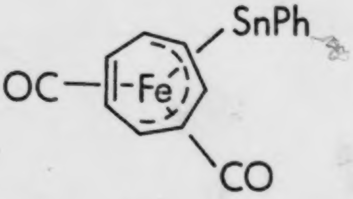
[e] See reference 82. No variable temperature ^{1}H NMR data have been reported for this compound; the temperature at which this spectrum was recorded has also not been specified.

[f] At 80°C this peak is still considerably broadened.

of the C_7H_7 ring in these complexes.[37,85] According to this line of thought the aromaticity of the C_7H_7 ligand in 58 is less pronounced than in the cationic iron and neutral manganese complexes listed in Table XXIII.

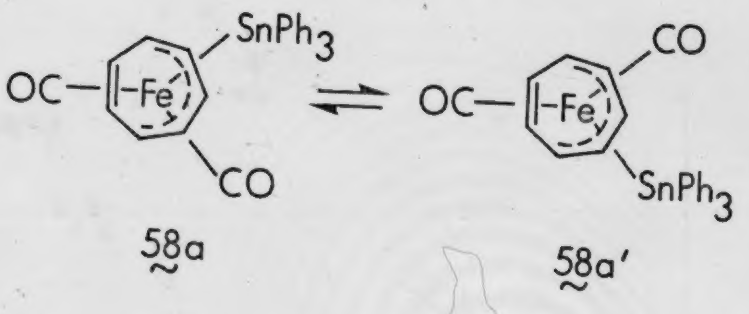
Due to the significant spin-coupling effects and the different line widths observed at -15°C the mechanism of the $Fe(CO)_2SnPh_3$ migration, i.e. a 1,2-, 1,3- or 1,4-shift, cannot be established on the basis of the ^1H NMR spectra. A 1,2-shift is most likely to occur in view of the results obtained for the other known η^5-C_7H_7 complexes.[37,81] Our attempts to simulate the spectra by means of the DNMR4 program[147] were frustrated by the strongly different linewidths of the four resonances. Assuming a 1,2-shift mechanism and identical relaxation times (T_2) for all protons of the seven-membered ring, collapse of the resonance due to H(4,4') is expected to occur at a slower rate than that of the other resonances (Chapters I and II). However, in the limiting spectrum for the ring-whizzing process in 58, at -15°C, the linewidth of the resonance due to H(4,4') is already much smaller than those of the other hydrogen resonances. No unambiguous assignment of the operative mechanism for this rearrangement can thus be made. Nevertheless, based on the similar nature of the present complex and the manganese derivative 59 it does not seem unreasonable to postulate that the rearrangement in 58 will also occur by 1,2-shifts of the $Fe(CO)_2SnPh_3$ moiety. Based on the similar chemical shift separations between the resonances in **58** and **59** and the almost identical coalescence temperatures in the two complexes the value of the activation energy in **58** is expected to be of comparable magnitude as well, i.e. ~63 kJ mol^{-1}. The corresponding values in $[(C_7H_7)Fe(CO)_3]^+$, **15**,[37] and $(C_7H_7)Fe(C_7H_9)$, **13**,[81] are 46 kJ mol^{-1} and 71 kJ mol^{-1}, respectively. The barrier to ring-whizzing thus increases in the order $[(\eta^5\text{-}C_7H_7)\text{-}Fe(CO)_3]^+ < (\eta^5\text{-}C_7H_7)Mn(CO)_3, (\eta^5\text{-}C_7H_7)Fe(CO)_2SnPh_3 < (\eta^5\text{-}C_7H_7)Fe(\eta^5\text{-}C_7H_9)$. The absence of a positive charge in the last three compounds and the absence of electron withdrawing carbonyl ligands in **13** establishes this order as the order of increasing backbonding to the C_7H_7 ring as well. The above data have been correlated with the difference in backbonding to the C_7H_7 ring.[37,85] In particular the presence of a vacant, low-lying acceptor orbital in the isoelectronic species of the type $(C_7H_7)\text{-}M(CO)_3{}^{y+}$, M = Mn, y = 0, and M = Fe, y = 1, is of importance.[85] Reduced backbonding is considered to result in an increase of the aromaticity of the C_7H_7 ring and the barrier for migration is reduced. This correlation accommodates the available experimental data even though the number of $\eta^5\text{-}C_7H_7$ complexes is confined to the five complexes listed in Table XXIII.

There is one additional feature of the variable temperature ^{1}H NMR spectra which requires our attention. Upon cooling of the sample below -15°C the resonances loose their fine structure and slowly collapse into the baseline. This is particularly evident for the resonances due to H(2,2') and H(3,3'). The limiting spectrum with respect to this second process could not be obtained and will only be observed at temperatures below -100°C at magnetic field strengths of 23,500 gauss (100 MHz) or less. It is clear that a second exchange process is still operative at -15°C. A rationale for this process can be found in the presence of a non-symmetrical ground state structure for the molecule $(\eta^5\text{-}C_7H_7)Fe(CO)_2SnPh_3$, e.g. 58a.



58a

Such an instantaneous structure would lead to the inequivalence of the protons 2 and 2', 3 and 3' and 4 and 4'. Proton 1 will be effected through the coupling with the protons 2 and 2' and might also exhibit a temperature dependent chemical shift position. Recalling the fact that the uncomplexed olefin is bent away from the metal one would anticipate the chemical shift difference of the protons 4 and 4' to be smaller than the chemical shift differences of the protons 2 and 2', and 3 and 3'. This means that different coalescence temperatures are to be expected for each of the three two-site exchange processes, i.e. the exchange of 2 with 2', 3 with 3', and 4 with 4'. As the chemical shift difference of H(4) and H(4') is probably smaller, the corresponding coalescence temperature will be lower and the resonance due to H(4,4') will remain sharp at temperatures where the other two resonances are already collapsing. This is indeed observed. As seen in Figure XXXVIII the resonance due to H(1) and H(4,4') are only slightly broadened at -70°C while the resonances due to H(2,2') and H(3,3') have almost disappeared into the baseline at this temperature. This exchange process seems best described as a rocking motion of the C_7H_7 ligand with respect to the $Fe(CO)_2SnPh_3$



moiety.* Such a motion will induce a plane of symmetry in the seven-membered ring which, at higher rates, results in the averaged spectrum seen at -15°C. Of course such a process is not observable for the tricarbonylmanganese and tricarbonyliron species discussed before. Similar processes have however been found for bis(cyclohexadienyl)-iron complexes[196,201] and, more recently, for the compounds 13[81] and 14.[82] A maximum value of 40 kJ mol^{-1} can be estimated for the energy of activation for this process from the NMR spectra.

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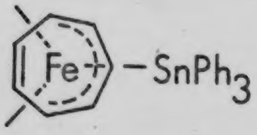
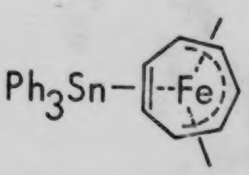
*Instead of this rocking motion one could consider a temperature dependent equilibrium of two symmetrical ground state structures, e.g. 58b and 58c. We do not



58b



58c

favor such an equilibrium in view of our inability to detect isomers in the infrared spectra of 58. Nonbonding interactions between the Ph_3Sn groups and the C_7H_7 ligand also do not appear to favor structure 58c.

e. Reactions with $P(OMe)_3$ and ^{13}CO, and a description of the attempts made to induce the migration of the $SnPh_3$ group to the C_7H_7 ring.

To test the lability of the carbonyl ligands in 22a the complex was irradiated for ~6 h in a pyrex well with a Hanovia 450-W lamp under an atmosphere of labeled carbon monoxide. The incorporation of ^{13}CO was then established by infrared spectroscopy. After recovery of crystalline 22a in 32% yield the extent of ^{13}CO incorporation was determined by mass spectroscopy as ~25%. This experiment shows that the dissociation of CO from 22a is a rather facile process and supports the arguments invoked before with respect to the synthesis of 57 and 58. In a similar experiment 22a was heated for more than seven days at ~80°C, or irradiated for over three days with a 100-W Mercury lamp in a sealed ^1H NMR tube. The irradiation or heating process was monitored by ^1H NMR spectroscopy. No decomposition or migration products could be detected. This lack of evidence for the migration of the Ph_3Sn moiety from iron to the cycloheptatrienyl ring is, of course, not surprising in view of the relative strengths of the iron-tin and tin-carbon bonds, as discussed in Chapter II.

The photochemical reaction of 22a with $P(OMe)_3$ in benzene for 48 h resulted, after removal of the solvent in a dark oil. Attempts to crystallize the products at low temperature failed but sublimation *in vacuo* yielded a small amount of a yellow solid which was identified by infrared spectroscopy and mass spectrometry as $Fe(CO)_3$-$(P(OMe)_3)_2$. It is evident that the substitution of the organic moiety in 22a by $P(OMe)_3$ is more favored under these conditions than the photochemical substitution of a carbonyl ligand. No other products could be identified.

Conclusions

The reactivity of the complexes (exo-7-$Ph_3GeC_7H_7$)-$Fe(CO)_3$ and $(\eta^3$-$C_7H_7)Fe(CO)_3SnPh_3$ has been examined.

$(\eta^4$-$C_7H_7GePh_3)Fe(CO)_3$ is thermally quite stable and unreactive towards triphenylphosphine (and ^{13}CO) at temperatures below 100°C. It is argued that steric interactions between the bulky *exo*-7-triphenylgermyl substituent and the incoming electrophile TCNE are, at least in part, responsible for the lack of adduct formation between 21c and TCNE. The formation of a charge transfer complex is inferred. It seems worthwhile to investigate the reactions of the same electrophile with the less sterically hindered complexes 21a and 21b.

A convenient route towards the synthesis of the molecule $Ph_3GeC_7H_7$ was envisioned *via* the disengagement of the $Fe(CO)_3$ group from this moiety. This was attempted *via* the action of trimethylamine oxide or triphenylphosphine upon 21c but neither reaction lead to the desired species. In contrast, $Ph_3GeOGePh_3$ was isolated from the reaction of 21c with trimethylamine oxide. The synthesis of $Ph_3GeC_7H_7$ is probably best accomplished by the direct interaction of $C_7H_7^+$ and Ph_3Ge^- at low temperature, in analogy to the recently reported improved synthesis of $Ph_3SnC_7H_7$.[35b] The relatively simple preparation of this latter molecule, in fairly good yield, suggests an attractive route towards the synthesis of the ring-substituted isomer of 22a, $(\eta^4\text{-}7\text{-}Ph_3SnC_7H_7)Fe(CO)_3$, as well. Use of the tricarbonyliron transfer reagents seems profitable here in view of the limited thermal and photochemical stability of $Ph_3SnC_7H_7$.[35] The reactions of $Ph_3MC_7H_7$, M = Si, Ge, and Sn, with $(BDA)Fe(CO)_3$ or $Fe_2(CO)_9$ could well result in the formation of *endo*-substituted derivatives of type 5. Reactions of substituted cycloheptatrienes with group VI metal carbonyl complexes are known to yield *endo*-substituted derivatives.[88]

The attempted synthesis of trans-$(OC)_3Fe(C_7H_7)Fe(CO)_3$-$SnPh_3$ *via* the reaction of 22a with pentacarbonyliron or with tricarbonyliron transfer reagents met with failure. However these reactions were not completely in vain as two novel fluxional compounds could be identified. Infrared, mass, and variable temperature ^1H and ^{13}C NMR data lend support to the presence of cis-$(OC)_3Fe(C_7H_7)Fe(CO)_2SnPh_3$. However this species could not be isolated pure in sufficient amounts. Red crystals of $(\eta^5\text{-}C_7H_7)Fe(CO)_2SnPh_3$ were also obtained and this compound was characterized. Two temperature dependent rearrangement processes were observed for the latter species by variable temperature ^1H NMR spectroscopy. The high temperature process, involving the migration of the $Fe(CO)_2SnPh_3$ moiety about the C_7H_7 ring, was easily established. In addition to this rearrangement a low energy rocking motion of the η^5-C_7H_7 moiety with respect to the $Fe(CO)_2SnPh_3$ unit was identified. To confirm these results ^{13}C NMR and X-ray crystallographic studies[143] are presently in progress. It is anticipated that these studies will allow the elucidation of the precise nature of the mechanism of the migratory shift of the $Fe(CO)_2$-$SnPh_3$ moiety, the accurate determination of the activation parameters for both fluxional processes and will provide the much needed structural information required for a better understanding of the factors controlling the stereochemically nonrigid behaviour of η^5-C_7H_7 transition metal derivatives.

The limited number of η^5-cycloheptatrienyl complexes known to date is surprising, while the lack of structural parameters for these compounds is disturbing. The fluxional character of η^5-C_7H_7 complexes is certainly as intriguing as that of the η^3-C_7H_7 compounds. Moreover, the former species appear to "perform their fluxional acts" at temperatures which are more amenable to NMR studies.

As $(\eta^5\text{-}C_7H_7)Fe(CO)_2SnPh_3$ and $(\eta^5\text{-}C_7H_7)Mn(CO)_3$ are both well-characterized molecules, $(\eta^5\text{-}C_7H_7)Mo(CO)_3SnPh_3$ could form the next addition to the still somewhat elusive class of $\eta^5\text{-}C_7H_7$ complexes.

CHAPTER SEVEN

EXPERIMENTAL PROCEDURES

Solvents and General Techniques

All reactions and operations were performed using Schlenk techniques under a static atmosphere of rigorously purified nitrogen.[202,203] Commercial nitrogen of 99.99% stated purity was passed through a heated column (90-100°C) containing BASF Cu-based catalyst (R3-11) to remove oxygen and a column of Mallinkrodt Aquasorb, which is P_2O_5 on an inert base, to remove water.

All glassware was heated in an oven to 95°C and then immediately evacuated and filled with nitrogen before any operation.

Solvents were dried by both refluxing and distilling from the appropriate drying agent under an atmosphere of nitrogen (Table XXIV). Pentane and ether were also freeze-thaw degassed before use. A number of solvents were preconditioned before being refluxed and distilled under nitrogen. Pentane was washed with concentrated H_2SO_4, until no colour developed in the acid layer, and water and dried over $MgSO_4$. Dichloromethane was washed with concentrated H_2SO_4 and water and dried over $CaSO_4$. Tetrahydrofuran was placed over molecular sieves for 24 hours, then refluxed and distilled from $LiAlH_4$ prior to the treatment with Na-K alloy/benzophenon.

TABLE XXIV

Drying Agents Used for Solvents

Solvent	Drying Agent
Toluene	Sodium metal
Pentane	Calcium hydride
Diethylether	Calcium hydride
Benzene	Potassium metal
Hexane	Potassium metal
Tetrahydrofuran	Sodium-potassium alloy benzophenone
Dichloromethane	Phosphorus pentoxide

Deuterated solvents were treated similarly and were vacuum-distilled onto dried molecular sieves and stored under nitrogen.

A silicon lubricant, Dow Corning High Vacuum Grease, was used on all ground glass joints.

Physical Measurements

Infrared spectra were recorded in the region 4000-250 cm^{-1} with a Perkin-Elmer 467 grating spectrometer or in the 2100-1700 cm^{-1} region on a Perkin-Elmer 337 grating spectrometer. In the latter case the spectra were recorded in expanded form on a Hewlett-Packard 7127A recorder. All spectra were measured using 0.5 or 1.0 mm NaCl and KBr cells and calibrated using a polystyrene film (PE 467) or gaseous carbon monoxide (PE 337). The infrared cells were equipped with serum stoppers, they were evacuated and then filled with nitrogen before use. The frequencies quoted are believed to be accurate to within 2(PE 467) and 0.5 cm^{-1} (PE 337), respectively.

Proton magnetic resonance spectra were obtained on the following spectrometers: Varian HA-100 (32°C), Varian HA-100 Digilab (32°C) and Perkin-Elmer R-32 (35°C). Variable temperature spectra were recorded on the Varian HA-100 or the Varian HA-100 Digilab spectrometers, using sealed or serum-capped NMR tubes. Specially adapted NMR sample tubes are commercially available from Wilmad Glass Co., Inc. (catalogue number 507-PP) and are supplied with an accompanying serum-cap. 5mm NMR tubes which had been attached to a 14/20 inner glass joint by the Glassblowing Division for this Department were employed in preparing sealed NMR samples. Sealed NMR tubes for high-temperature spectra were tested at the appropriate temperature range before they were sumitted to the NMR laboratory. For both the high-temperature spectra requiring toluene-d_8 as solvent and the low-temperature spectra requiring, for example, a CHF_2Cl/CD_2Cl_2 solvent mixture, the sample was prepared on the vacuum line and the NMR tube sealed under high vacuum. Temperature calibration was achieved with a copper/Constantan thermocouple with one junction immersed in ice water and the other in the NMR probe below the sample tube. The ^1H NMR chemical shifts were measured relative to TMS or to the internal solvent resonance. The following conversions were used:[209]

$$\delta_{TMS} = \delta_{CHDCl_2} - 5.32 \text{ ppm}$$

$$\delta_{TMS} = \delta_{C_6D_6CHD_2} - 2.09 \text{ ppm}$$

$$\delta_{TMS} = \delta_{THF(H_{2,5})} - 3.58 \text{ ppm}$$

$$\delta_{TMS} = \delta_{CHCl_3} - 7.24 \text{ ppm}$$

Carbon-13 NMR spectra were recorded on a deuterium-lock Bruker HFX-90/Nicolet 1085 FT or a Bruker WP-60 FT spectrometer. The former operates at 22.628 MHz, the latter at 15.086 MHz. For variable temperature work, depending on the solvent and the temperature, serum-capped or sealed 10 mm o.d. tubes were employed. NMR samples were sealed *in vacuo*. In these cases the ^{13}C NMR tubes had been attached to a 14/20 inner glass joint which allowed the convenient filling and sealing of the NMR tubes. Samples were tested at the appropriate temperatures before being submitted for high-temperature NMR work. Temperature measurements and calibration were made with a Bruker temperature control unit, Model B-5T 100/700 and are believed to be accurate to ±1°K. The ^{13}C NMR chemical shifts were measured relative to TMS or to the internal solvent resonance. In the latter case the following conversions were used:[207,208]

$$\delta_{TMS} = \delta_{CHDCl_2} - 53.63 \text{ ppm}$$

$$\delta_{TMS} = \delta_{THF(C_{2,5})} - 68.05 \text{ ppm}$$

$$\delta_{TMS} = \delta_{C_6D_5\underline{C}D_3} - 20.4 \text{ ppm}$$

Forsén-Hoffmann experiments were carried out as described in Chapter II. Good reviews of the experimental procedures, the assumptions involved, and the sources of error are available.[25,31] [illegible] interval of at least

$5T_1$ between pulses was applied. T_1 relaxation times were measured by the usual $(180-\tau-90-(\text{sample})-5T_1)$ pulse sequence.

Simulation of the spectra was achieved by use of the program DNMR4.[147] The rates were determined by visual comparison of the observed and calculated spectra. Activation parameters were extracted by a least-square plot of ln(rate/T) versus 1/T. Using the Eyring equation of absolute reaction rate theory $\Delta H^{\dagger}$ and $\Delta S^{\ddagger}$ can thus be extracted. A value of 1.0 was assumed for the transmission coefficient κ. Temperatures, rates and activation parameters are presented in tabular form in the appropriate sections of this Chapter. Estimates of the error limits in the values of $\Delta G^{\ddagger}$ are based on the root-mean-square errors observed in the slope $(= \Delta H^{\ddagger}/R)$ and the intercept $(=23.760 + \Delta S^{\ddagger}/R)$ of the straight line obtained by the above least-square analysis.

Mass spectra were recorded on an Associated Electrical Industries MS-12 mass spectrometer, usually operating at 70 eV. The samples were introduced into the ion source using the direct inlet technique at a temperature just sufficient to record the data. Field ionization mass spectra were recorded on an AEI-MS-9 spectrometer. The natural abundances of the isotopes of the elements discussed in the Chapters II through VI, C, H, O, Fe, Si, Ge, Sn, Pb, Au, P, and W, are shown in Table XXV.[121]

TABLE XXV

Natural abundances of the isotopes of the elements discussed in the Chapters II through VI.

Element	C Atomic number = 6				
Masses	12.00000	13.00335			
Abundances	98.890%	1.100%			
Sum of Abundances = 100.000%					
Element	H Atomic Number = 1				
Masses	1.00783	2.01410			
Abundances	99.985%	0.015%			
Sum of Abundances = 100.000%					
Element	O Atomic number = 8				
Masses	15.99491	16.99911	17.99915		
Abundances	99.759%	0.037%	0.204%		
Sum of Abundances = 100.000%					
Element	Fe Atomic number = 26				
Masses	53.93961	55.93492	56.93438	57.93326	
Abundances	5.820%	91.660%	2.190%	0.330%	
Sum of Abundances = 100.000%					
Element	Si Atomic number = 14				
Masses	27.97693	28.97649	29.97375		
Abundances	92.210%	4.700%	3.090%		
Sum of Abundances = 100.000%					
Element	Ge Atomic number = 32				
Masses	69.92427	71.92174	72.92336	73.92114	75.92136
Abundances	20.560%	27.420%	7.790%	36.470%	7.760%
Sum of Abundances = 100.000%					

continued...

TABLE XXV (Continued)

Element	Sn Atomic number = 50				
Masses	111.90494	113.90295	114.90352	115.90210	116.90305
Abundances	0.950%	0.650%	0.340%	14.240%	7.570%
	117.90178	118.90338	119.90211	121.90340	123.90523
	24.010%	8.580%	32.970%	4.710%	5.980%
Sum of Abundances = 100.000%					
Element	Pb Atomic number = 82				
Masses	203.97307	205.97446	206.97589	207.97664	
Abundances	1.400%	25.200%	21.700%	51.700%	
Sum of Abundances = 100.000%					
Element	Au Atomic number = 79				
Masses	196.96654				
Abundances	100.000%				
Sum of Abundances = 100.000%					
Element	P Atomic number = 15				
Masses	30.97375				
Abundances	100.000%				
Sum of Abundances = 100.000%					
Element	W Atomic number = 74				
Masses	179.94698	181.94826	182.95029	183.95099	185.95433
Abundances	0.140%	26.410%	14.400%	30.640%	28.410%
Sum of Abundances = 100.000%					

Melting points are uncorrected and were determined on a Thomas-Hoover apparatus on samples which were sealed in a capillary.

Analyses were performed by the Microanalytical Laboratory of this department or at the Analytische Laboratorien, Engelskirchen, West-Germany.

Reagents and Preparations, Chapter II.

Iron pentacarbonyl was purchased from Ventron Corporation and filtered before use. Cycloheptatriene (Aldrich), triphenylgermanium bromide (Strem Chemicals), triphenyllead chloride (Strem Chemicals), trimethylgermanium bromide (Ventron Corporation), trimethylchlorosilane (Pierce), chloromethyltrimethylsilane (PCR), tri(n-butyl)-tin chloride (Alfa), and triphenyltin chloride (Ventron Corporation) were used as received. Triphenylchlorosilane, free of the hydroxide, was supplied by Dr. J. Anglin. Potassium hydride (Alfa) was freed from the paraffin oil, in which it was received, by washing with hexane. This was repeated twice after which the residual hexane was removed *in vacuo*.

Bis(triphenylphosphine)iminium chloride was prepared according to the method of Ruff and Schlientz,[167] following an improved procedure.[204] Florisil (60-100 mesh) was used as received from Fischer Scientific, alumina of activity II was prepared from "Alumina Catalyst"

(Harshaw Chemical) by treatment with ethyl acetate, methanol and water, followed by drying at 130°C. Carbon monoxide, 90% enriched in ^{13}CO, was purchased from Monsanto Research Corporation. Potassium t-butoxide was prepared from t-butanol and potassium. The compound was sublimed and stored under nitrogen, and was resublimed just prior to use.

Preparation of $(C_7H_8)Fe(CO)_3$.

This compound was prepared by the method of Kruczynski[205] as follows. Cycloheptatriene (50 ml, b.p. 115.5°C) and ironpentacarbonyl (50 ml, b.p. 102°C) were dissolved in 100 ml methylcyclohexane (b.p. 100°C) and refluxed, with efficient stirring, for 3 days. After cooling to room temperature the solvent and excess reactants were removed under vacuum. Cycloheptatriene-tricarbonyliron was then distilled twice (60-70°C, .1 mm Hg)[68,69,118] and stored under nitrogen. Yield 60-65%. Other synthetic procedures have been reported,[68,69,106,118] but the above method, based on the yields obtained in these laboratories or the simplicity of the procedure, seems superior. For comparison and reference the ^1H NMR spectra of C_7H_8 [206] and $(C_7H_8)Fe(CO)_3$, the latter in three different solvents, are shown in Figures XXXIX and XXXX, respectively.

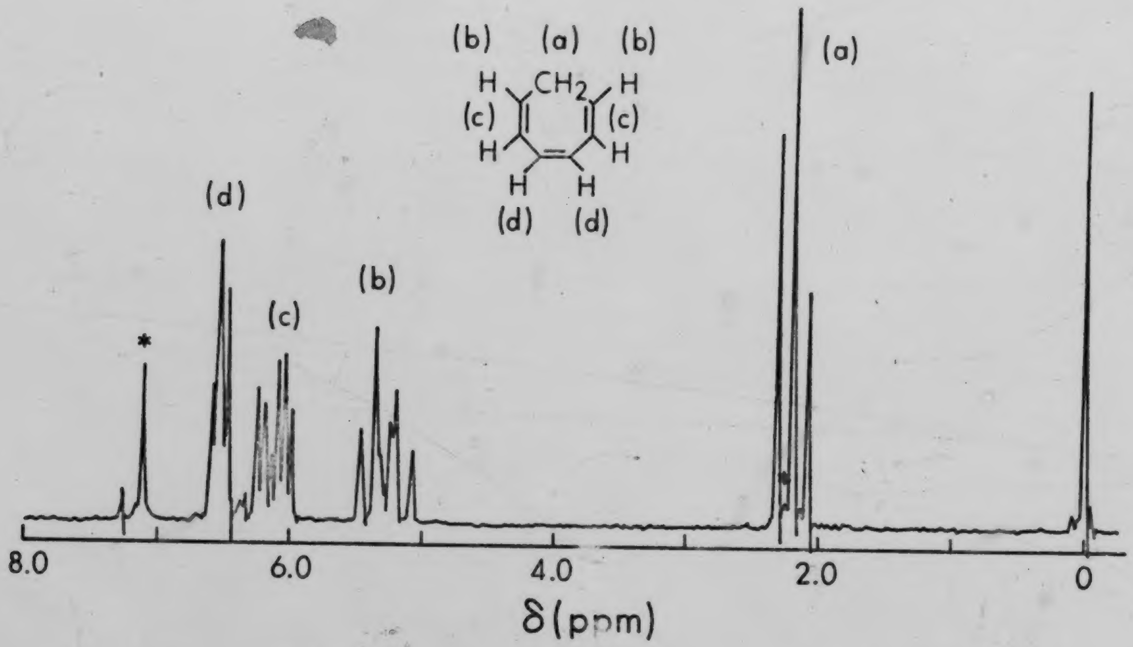


Figure XXXIX. ^{1}H NMR spectrum of cycloheptatriene ($\underset{\sim}{1}$).[206]

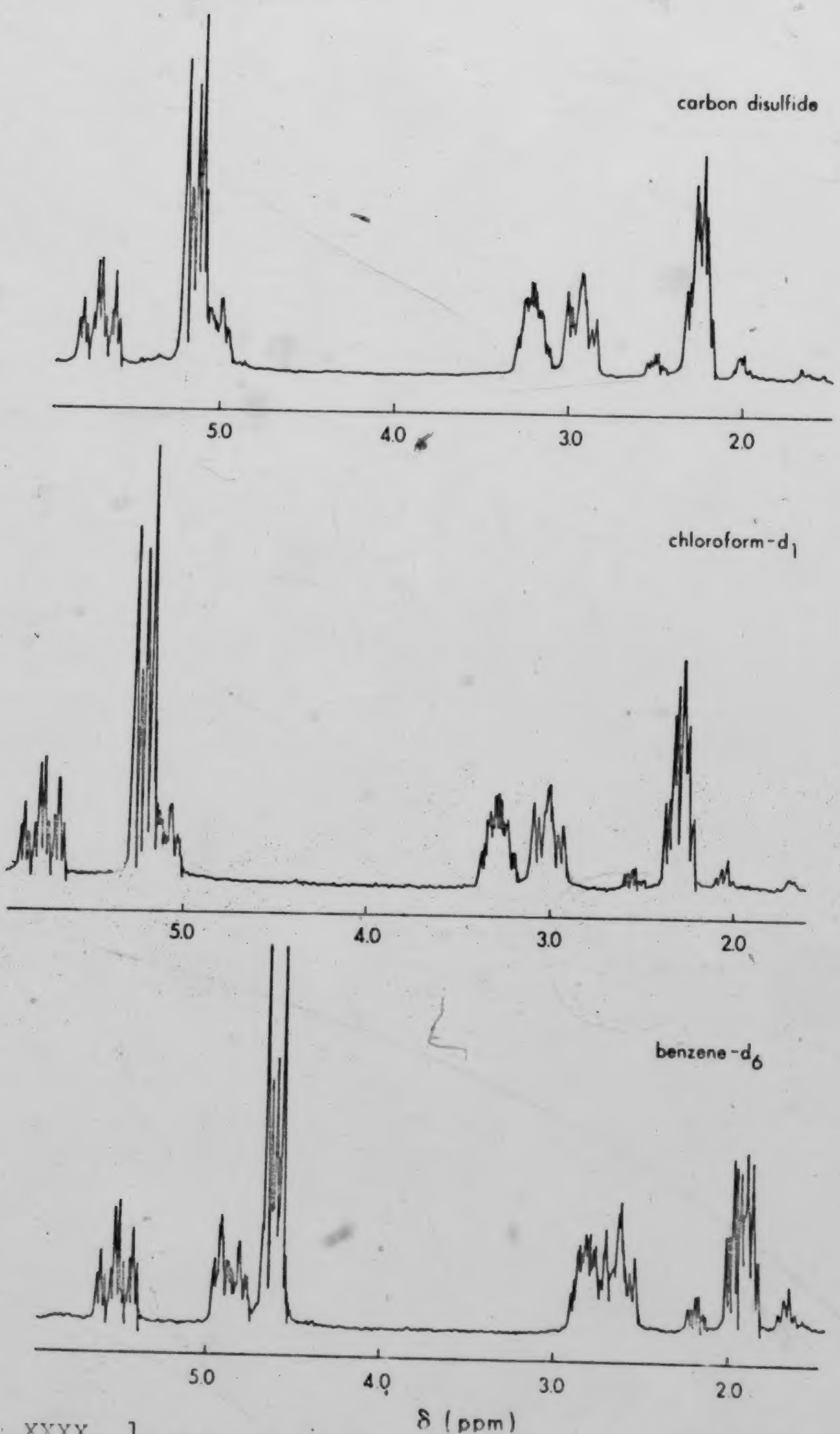


Figure XXXX. ^{1}H NMR spectra of (cycloheptatriene)-Fe(CO)$_3$ (2) at ambient temperature.

Preparation of potassium cycloheptatrienyltricarbonyl ferrate (-I).

Extremely air-sensitive solutions of this compound were prepared by a method similar to the preparation of $(Li[(C_7H_7)Fe(CO)])$.[105,112] A typical procedure is as follows: 3.60 g (15.52 mmol) $(C_7H_8)Fe(CO)_3$ dissolved in 50 ml of THF was added dropwise to a magnetically stirred slurry of 1.71 g (15.27 mmol) t-BuOK in 50 ml of THF, the resulting dark red solution was stirred for 14 h and subsequently used for further reactions. The formation of the anion $[(C_7H_7)Fe(CO)_3]^-$ can be followed conveniently by infrared spectroscopy. The absorption bands due to $(C_7H_8)Fe(CO)_3$ (2048(s), 1974(s,br), in THF) rapidly decrease in intensity while new intense bands at 1942(vs) and 1868 (vs, br) appear. Removal of all volatile components under vacuum leaves $[(C_7H_7)Fe(CO)_3]^-K^+$ as a red pyrophoric solid material. ^1H NMR spectra in THF-d_8 show the presence of one molecule of THF per anion even after prolonged evacuation at ambient temperature.

The extreme air sensitivity of this anion prevented its characterization by elemental analysis. However, the spectroscopic measurements conclusively prove its formation and we believe the absence of other peaks in the IR and NMR spectra bespeak for its purity. In subsequent reactions it is also assumed that anion $\underset{\sim}{16}$ is formed quantitatively with no other iron-containing byproduct. The calculations of the amounts of reagents needed to react with **16** are based on this assumption.

Deprotonation of $(C_7H_8)Fe(CO)_3$ by potassium hydride.

Upon the addition of an equimolar amount of **2** to a slurry of "pure" KH (.110 g, 2.75 mmol) in 50 ml of THF a red solution formed while dihydrogen evolved. The reaction was followed by infrared spectroscopy and was complete within minutes. However, it was found that the available KH was unreliable as different samples from new, freshly opened, bottles resulted in induction periods of 0.2-4.0 h, while the deprotonation of **2** was incomplete with long induction times. Once opened, the sample of KH would rapidly loose its deprotonating function and no red coloration would occur. Thus a simple preparation of **16** could not be relied upon and t-BuOK remained the most convenient deprotonating agent.

Preparation of (7-triphenylgermylcycloheptatriene)tricarbonyliron.

A solution of **16** (15.04 mmol) in 50 ml of THF was added dropwise over a period of 4 h to a magnetically stirred solution of 5.77 g (15.04 mmol) Ph_3GeBr. After the addition was completed, the resulting yellow-brown solution was allowed to stir for an additional 2 h. Solvent was removed under vacuum and extraction of the residue with 300 ml of hexane or pentane gave a yellow solution. This solution was filtered and slowly concentrated until yellow crystals started to form. Further cooling (4°C) afforded (7-$Ph_3GeC_7H_7$)$Fe(CO)_3$ (4.72 g, 59%). No attempts were made to optimize the yield. Recrystallization from hexane yielded an analytically pure sample which decomposed above 130°C.

Anal. Calcd. for $C_{28}H_{22}O_3GeFe$: C, 62.92; H, 4.12. Found: C, 62.98; H, 4.18.

No ^{13}CO enrichment was observed on heating (7-$Ph_3GeC_7H_7$)-$Fe(CO)_3$ in toluene at 100° and for 24 h under an atmosphere of labelled carbon monoxide.

Various amounts of bis(triphenylgermyl)ether, $Ph_3GeOGePh_3$, were obtained in this reaction. All attempts to separate $Ph_3GeOGePh_3$ and **21c** chromatographically (alumina of activity II, florisil) failed, only fractional crystallization from hexane proved successful to obtain pure product (as evidenced by a correct integration ratio in the ^1H NMR spectra (phenyl/ring = 15/7) and the absence of $Ph_3GeOGePh_3$ in the mass spectra).

Preparation of ($Me_3GeC_7H_7$)$Fe(CO)_3$ and ($Me_3SiC_7H_7$)$Fe(CO)_3$.

These compounds were synthesized and purified according to the procedure outlined above for ($Ph_3GeC_7H_7$)-$Fe(CO)_3$. No traces of $Me_3SiOSiMe_3$ or $Me_3GeOGeMe_3$ could be detected. The yellow ($Me_3GeC_7H_7$)$Fe(CO)_3$ can also be purified by sublimation *in vacuo* (10^{-4} mm Hg) at 60°C.

Various amounts of the dimeric product $[(C_7H_7)Fe(CO)_3]_2$ were also obtained in these preparations and were separated from the complexes 21 by chromatography on alumina of activity II. Yields were comparable to those in the synthesis of 21c (45-55%).

Anal. Calcd. for $C_{13}H_{16}O_3GeFe$: C, 44.78; H, 4.63. Found: C, 44.96; H, 4.65.

Anal. Calcd. for $C_{13}H_{16}O_3SiFe$: C, 51.33; H, 5.30. Found: C, 51.61; H, 5.40.

Preparation of (η-1-3-cycloheptatrienyl)triphenylstannyltricarbonyliron.

A solution of $(K[(C_7H_7)Fe(CO)_3])$ (12.93 mmol) in 50 ml of THF was added dropwise over a period of 2.5 h to a magnetically stirred solution of 4.84 g (12.57 mmol) of $(C_6H_5)_3SnCl$ in 100 ml of THF. After the addition was completed the reaction mixture was allowed to stir overnight. Solvent was removed from the resulting dark red solution under vacuum and 100 ml of hexane was added to the residue. The red solution was filtered and concentrated to approximately 40 ml. Crystallization at dry ice-acetone temperature gave red crystals of $(C_7H_7)Fe(CO)_3$-$(Sn(C_6H_5)_3)$ in about 60% yield. Recrystallization from pentane at 4°C gave an analytically pure sample melting at 122-123°C.

Anal. Calcd. for $C_{28}H_{22}O_3SnFe$: C, 57.93; H, 3.79; O, 8.28.
Found: C, 57.96; H, 3.84; O, 8.20.

Various amounts of $Ph_3SnOSnPh_3$ were obtained in this reaction. The desired compound could easily be freed from this impurity by fractional crystallization. (C_7H_7)-$Fe(CO)_3SnPh_3$ decomposed upon chromatography on florisil (hexane) or alumina (activity II, hexane or benzene) but could be chromatographed on a short silica gel column with benzene as eluent.

Preparation of (η-1-3-cycloheptatrienyl)triphenyllead-tricarbonyliron.

The reaction was carried out as described for complex 22a by utilizing 7.41 mmol of $[(C_7H_7)Fe(CO)_3]^-K^+$ in 40 ml of THF and 3.20 g (6.75 mmol) of triphenyllead chloride in 80 ml of THF. The residue was extracted with 50 ml of toluene and the red solution was filtered. After reducing the volume to ~20 ml under vacuum, 50 ml of hexane were added and the solution was filtered over Celite. Cooling (-15°C) gave $(C_7H_7)Fe(CO)_3PbPh_3$ as dark red crystals in about 40% yield which could be recrystallized from a toluene/hexane (1/2) solvent mixture.

Anal. Calcd. for $C_{28}H_{22}O_3PbFe$: C, 50.22; H, 3.29; O, 7.17.
Found: C, 49.94; H, 3.35; O, 7.40.

TABLE XXVI

Activation Parameters obtained from the ^{1}H NMR spectra of $(\eta^3\text{-}C_7H_7)Fe(CO)_3SnPh_3$ for the 1,2-$Fe(CO)_3SnPh_3$ shift.

T,°C	k, sec^{-1}	Activation Parameters
-105	1.0	$\Delta G^{\dagger}_{-60°} = 40.5$ kJ mol^{-1}
-95	4.0	
-80	39.0	$\Delta H^{\ddagger} = 40.5$ kJ mol^{-1}
-75	83.0	
-70	100.0	$\Delta S^{\ddagger} = 0.20$ J T^{-1} mol^{-1}
		correlation coeff. -0.9979

TABLE XXVII

Activation Parameters from the ^1H NMR spectra of $(\eta^3\text{-}C_7H_7)\text{-}Fe(CO)_3PbPh_3$ for the 1,2-$Fe(CO)_3PbPh_3$ shift.

T, °C	k, sec^{-1}	Activation Parameters
-95	0.1	$\Delta G^{\ddagger}_{-70} = 45.8$ kJ mol^{-1}
-80	1.0	
-70	8.0	$\Delta H^{\ddagger} = 46.9$ kJ mol^{-1}
-60	30.0	
-30	600.0	$\Delta S^{\ddagger} = 5.5$ J T^{-1} mol^{-1}
		correlation coeff. -0.9973

The reaction of $[(C_7H_7)Fe(CO)_3]^-$ with $(n\text{-}Bu)_3SnCl$.

The reaction of 16 with tri(n-butyl)tin chloride was carried out at ambient temperature. 13.5 mmol of 16 in 60 ml of THF was slowly added to a stirred solution of $(n\text{-}Bu)_3SnCl$ (~4.0 ml; 3.64 ml is required as a stoichiometric amount) in 60 ml of THF. The procedure followed and the work-up of the reaction mixture was similar to that described for the reaction of 16 with Ph_3SnCl. A red oil resulted. A yellow-orange oil could be distilled from the oily residue (0.025 mm Hg, $T \leq 60°C$) and was identified as a mixture of $(C_7H_8)Fe(CO)_3$ and $(n\text{-}Bu)_3SnCl$ by its infrared- and nmr spectra. The solution infrared spectra of the resulting red oil in hexane showed several carbonyl stretching frequencies at 2055, 2050, 2038, 1990, 1983, 1978, 1969, and 1947. The ν_{CO} bands at 2055, 1990, and 1978 are assigned to $(C_7H_8)Fe(CO)_3$ while the remaining 5 frequencies are assigned to the isomers 21 and 22, with $R_3M = (n\text{-}Bu)_3Sn$. An approximately 1:1 mixture of $[\eta^4\text{-}(n\text{-}Bu)_3SnC_7H_7]Fe(CO)_3$, 21e, and $(\eta^3\text{-}C_7H_7)Fe(CO)_3\text{-}Sn(n\text{-}Bu)_3$, 22c, is evident on the basis of the intensities of the infrared absorptions. Both the positions and the intensities of the ν_{CO} frequencies are very similar to those of the reported mixture of $[\eta^4\text{-}Me_3SnC_7H_7]Fe(CO)_3$, 21f, and $(C_7H_7)Fe(CO)_3SnMe_3$, 22d.[41a]

The ^1H NMR spectra of this oil have been discussed in Chapter II. At δ 5.20 a sharp resonance is observed for the ring protons in 22c, which broadens at lower temperatures. The signal has coalesced at ca. -50°C while new resonances are visible below -80°C. Unfortunately these new peaks are partially obscured by the resonances due to the ring-substituted isomer $((n\text{-Bu})_3SnC_7H_7)Fe(CO)_3$. The presence of the n-butyl substituents on the tin atom further complicates the low temperature ^1H NMR spectra. These results are analogous to those obtained from the reaction of 16 with Me_3SnCl.[152]

The reaction of $[(C_7H_7)Fe(CO)_3]^-$ with Me_3SnCl.

The reaction of anion 16 with trimethylchlorotin was repeated after earlier attempts to prepare $(Me_3SnC_7H_7)$-$Fe(CO)_3$ had only resulted in a mixture of 21f and 22d.[41a,152] The reaction was carried out at ambient temperature in THF employing 21.7 mmol of 16. Work-up procedures were as described for the reaction of 16 with $(n\text{-Bu})_3SnCl$. A red oil resulted and infrared spectra indicated the presence of the two isomers 21f and 22d. Attempted column chromatographic separations at ambient temperature led only to decomposition and recovery of $(C_7H_8)Fe(CO)_3$.

The interaction of $[(C_7H_7)Fe(CO)_3]^-$ with chlorotriphenylsilane.

4.74 mmol $[(C_7H_7)Fe(CO)_3]^-$ in 20 ml of THF was added dropwise to chlorotriphenylsilane (1.55 g, 5.23 mmol) in 20 ml of THF at ambient temperature. No decolouration was observed and infrared spectra showed the continued presence of $[(C_7H_7)Fe(CO)_3]^-$.

The interaction of $[(C_7H_7)Fe(CO)_3]^-$ with Me_3SiCH_2Cl.

14.28 mmol of $[(C_7H_7)Fe(CO)_3]^-$ in 60 ml of THF was slowly added over a period of 3 h to a magnetically stirred solution of Me_3SiCH_2Cl (2.1 ml, 1.85 g, 20.0 mmol) in 60 ml of THF. No decolouration of the red anion solution was observed. After stirring the solution for 24 hrs at ambient temperature infrared spectra indicated the presence of 16 only.

Reagents and Preparations, Chapter III.

Triphenylphosphine (Aldrich) and chloroauric acid ($HAuCl_4$, Alfa) were used as received. $W(CO)_4(NO)Br$ was kindly supplied by Professor P. Legzdins of the University of British Columbia and used as received. Diphenylchlorophosphine was purchased from Alfa and used without further purification.

Preparation of (triphenylphosphine)gold chloride.

$(C_6H_5)_3PAuCl$ was prepared according to the procedure of Davison and Ellis as follows.[156b,*]
2.52 g (9.61 mmol) triphenylphosphine in 50 ml of ethanol (95%) is heated to ca. 50°C until all the phosphine has

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[*] Some (typing) errors are apparent in the relevant experimental section of reference 156b.

dissolved. The warm solution is then poured into a stirred yellow solution of 2.0 g (5.08 mmol) chloroauric acid ($HAuCl_4.3H_2O$) in 75 ml of ethanol. After 60-90 sec a white precipitate is formed. The mixture is stirred for an additional 2-3 h and thereafter the solution is filtered, the white powder collected, washed twice with 15 ml of ethanol and dried under vacuum. Yield: 2.0 g (80%) of Ph_3PAuCl.

Anal. Calcd. for $C_{18}H_{15}PAuCl$: C, 43.70; H, 3.06. Found: C, 43.89; H, 3.08.

The reaction of Ph_3PAuCl with $[(C_7H_7)Fe(CO)_3]^-$.

A solution of 16 (6.34 mmol) in 60 ml of THF was slowly (3 h) added to a magnetically stirred solution of Ph_3PAuCl (3.14 g, 6.35 mmol) in 60 ml of THF at ambient temperature. The mixture was stirred for 48 h during which time small shiny particles appeared (presumably metallic gold, *vide infra*) in addition to a large amount of a fluffy brown precipitate. Various reaction times did not change the course or the yield of the reaction.

An infrared spectrum of the so obtained THF solution showed ν_{CO} bands at 1986(s), 1964(m), 1944(s), 1923(m), 1901(m), 1870(s,br), and 1846(sh) cm^{-1}. The somewhat broad absorption at 1870 cm^{-1} is believed to be due to 16 which would also establish the origin of the band at 1944 cm^{-1}. The absence of any absorptions attributable to $(C_7H_8)Fe(CO)_3$ is to be noted. In an attempt to consume all the anion the mixture was stirred for another 48 h (no change in the infrared spectra was observed at this point) and the solvent then removed under reduced pressure. 60 ml of toluene was added to the remaining red oil and the solution stirred overnight and filtered. A red oil separated from this filtrate at 4°C. Infrared spectra of the filtrate in toluene showed the absence of any carbonyl stretching bands assignable to 16 (absorptions at 2047(s), 2034(sh), 2066(s), 1973(s,br), 1924(s), and 1900(m) cm^{-1}). Removal of the supernatant and addition of varying amounts of dichloromethane, toluene and/or hexane with appropriate cooling and/or concentrating of the obtained mixtures failed to produce a crystalline or solid material. In many cases a fluffy brown precipitate would result while the walls of several three-neck flasks became coated with a thin layer of metallic gold. Many similar attempts to induce crystallization produced identical results. One component of the brown precipitate could be identified by its infrared- and mass spectra as $(Ph_3P)_2Fe(CO)_3$.

One particular reaction produced a tiny amount of a red solid which analyzed well for $(C_7H_7)Fe(CO)_3AuPPh_3$. Anal. Calcd. for $C_{28}H_{22}O_3PFeAu$: C, 48.70; H, 3.19; P, 4.49; Au, 28.55. Found: C, 48.55%; H, 3.32; P, 4.47; Au, 28.46. A ^1H NMR spectrum in CD_2Cl_2 of a similar but less pure sample showed a sharp resonance at δ5.16 ppm for the hydrogens of the seven membered ring. Interestingly, this signal did not broaden significantly between +30° and -90°C. However, at lower temperatures the resonance broadened and collapsed into the baseline at ~-130°C.

The reaction of $[(C_7H_7)Fe(CO)_3]^-$ with $[W(CO)_2(NO)(THF)Br]_2$.

A THF solution (60 ml) containing $W(CO)_4(NO)Br$ (1.36 g, 3.35 mmol) was stirred at ambient temperature for 14 h. The initially yellow solution turned orange and infrared spectra showed the absence of carbonyl stretching vibrations due to the starting material. The solvent was removed *in vacuo* to give a yellow-orange solid, which was redissolved in 50 ml of CH_2Cl_2. To this magnetically stirred solution a second solution of $PPN^+[(C_7H_7)Fe(CO)_3]^-$ (2.78 mmol, 2.14 g) in 50 ml of CH_2Cl_2 was added dropwise, at ambient temperature. The reaction could conveniently be followed by infrared spectroscopy, after stirring the reaction mixture for 60 h no absorptions attributable to 16 could be observed. The solvent was removed *in vacuo*. The residue was then treated as follows.

(a) 35 ml of toluene was added to the red-brown residue. The resulting orange solution was filtered, concentrated and crystallization was attempted. Because no crystallization could be induced the solvent was again removed *in vacuo* and the oily orange residue was chromatographed over florisil with diethyl ether as eluent.

Only one orange band could be eluted. Removal of the diethyl ether resulted in the formation of a red oil and some red crystals. Repeated crystallization from hexane produced a small amount of red solid. Infrared spectra in hexane showed ν_{CO} at 2052(s), 1988(s), 1977(s), 1925(s), and 1901(s). The ^{1}H NMR spectrum (100 MHz) exhibited resonances at δ2.96(m,~3H), 5.11(d), 5.38(m), and 5.59(t or dd) (together ~4H).

(b) After the extraction of the original reaction mixture with toluene, as described under (a), 30 ml of tetrahydrofuran was added to the residue and the solution was filtered to remove a very small amount of undissolved material. Cooling and/or the addition of hexane did not yield any precipitate. Removal of the solvents *in vacuo* resulted in a dark red oil. Chromatography on florisil (eluent: ether/THF or dichloromethane) caused extensive decomposition and resulted only in the isolation of a small amount of $(C_7H_8)Fe(CO)_3$. Attempts to sublime components of the reaction mixture under high vacuum (10^{-4} mm Hg, $T \leq 50°$) onto a water (or dry ice/acetone) -cooled probe were also unsuccessful.

The reaction of $[(C_7H_7)Fe(CO)_3]^-$ with Ph_2PCl.

A THF solution (60 ml) of $[(C_7H_7)Fe(CO)_3]^-$ (8.55 mmol) was added dropwise to a magnetically stirred solution of Ph_2PCl (1.36 g, 6.17 mmol) in 50 ml of THF over a period of 1.5 h at 0°C. The red anion solution immediately turned yellow upon contact with the chlorodiphenylphosphine solution. The resulting orange-yellow mixture was stirred overnight, concentrated to a final volume of 70 ml and filtered. 140 ml of pentane was added to the filtrate and upon cooling at -10°C a small amount of yellow precipitate formed. Two different work-up procedures are outlined below.

(a) The yellow solid was filtered off and characterized by infrared and NMR spectroscopy, mass spectrometry, and elemental analysis.
Anal. Calcd.: see Table XXVIII. Found: C, 60.35; H, 4.29, ν_{CO} (pentane, cm^{-1}): 2047(s)*, 2028(m), 1986(s), 1974(s)*, 1964(m), and 1936(m). Frequencies designated with an asterisk are assigned to 23.

(b) Solvents were removed from the filtrate *in vacuo*. All attempts to crystallize the resulting organic-red oil failed to produce a solid material. Chromatography over alumina (eluent: benzene or dichloromethane) resulted in the isolation of only one yellow fraction which was identified by its infrared spectrum. The positions and relative intensities of the ν_{CO} absorptions observed were identical to those described for the yellow powder in (a) and no separation had thus been achieved. A different fraction of the remaining oil was placed in a sublimation apparatus, the material decomposed at T $\simeq$ 130°C (10^{-4} mm Hg,

TABLE XXVIII

Calculated analytical composition of some possible products from the reaction of $[(C_7H_7)Fe(CO)_3]^-$ with Ph_2PCl.

Compound	Elemental Composition		
	%C	%H	%O
$\underset{\sim}{2}$	51.77	3.48	20.69
$\underset{\sim}{23}$	51.99	3.05	20.78
$(Ph_2PC_7H_7)Fe(CO)_3$	63.49	4.12	11.53
$(Ph_2PC_7H_7)Fe(CO)_2$	64.98	4.41	8.24
$(Ph_2PC_7H_7)Fe(CO)_4$	62.19	3.86	14.41
$[(Ph_2PC_7H_7)Fe(CO)_2]_2$	64.98	4.41	8.24

probe at -78°C) while only a small amount of oil sublimed onto the probe. Infrared spectra showed the presence of the same 6 ν_{CO} bands as above but for the ν_{CO} bands assigned to 53 which were more intense.

Reagents and Preparations, Chapter IV

The compounds $(Ph_3GeC_7H_7)Fe(CO)_3$, PPNCl, and t-BuOK were synthesized as outlined above. Triphenyltin chloride (Ventron Corporation) and trimethylchlorosilane (Pierce) were used as received. Deuterium chloride (Merck Sharp & Dohme, 99.9% stated purity) was bubbled through an Et_2O solution for 0.25 h. A 10 ml aliquot of this solution (usually 60 ml) was taken and added to a beaker containing 10 ml of H_2O. The resulting solution was then titrated with a NaOH solution of known molarity. Identical procedures were followed with hydrogen chloride gas (Matheson).

The ^1H NMR spectrum of $[(Ph_3GeC_7H_6)Fe(CO)_3]^-$ was simulated by use of the program ITRCAL available from Nicolet Instrument Corporation (Madison, Wisconsin; 1974).

Preparation of $[(Ph_3GeC_7H_6)Fe(CO)_3]^-$.

Addition of 21c (1.12 g, 2.1 mmol) dissolved in 45 ml of tetrahydrofuran to a slurry of t-BuOK (.25 g, 2.2 mmol) in 20 ml of tetrahydrofuran at ambient temperature resulted in the formation of an air-sensitive deep red solution (ν_{CO}: 1938 and 1864 cm^{-1}). Upon removal of the solvent from this solution *in vacuo* a red solid was obtained. After removing all volatiles the solid was redissolved in 50 ml of THF, an equimolar amount (or an excess) of PPNCl was added to the red solution. After stirring the mixture magnetically for 72 h, the solution was filtered and the solvent removed *in vacuo*.

Preparation of (triphenylgermylcycloheptatrienyl)(triphenyltin)tricarbonyliron, $(\eta^3\text{-}Ph_3GeC_7H_6)Fe(CO)_3SnPh_3$.

2.04 mmol (1.09 g) of 21c was dissolved in 30 ml of tetrahydrofuran. This solution was added dropwise to a suspension of 0.23 g (2.05 mmol) of t-BuOK in 35 ml of THF. The red solution was stirred overnight at ambient temperature. THF was then removed *in vacuo* and the red solid was dried. After redissolving the solid, the solution was added dropwise to a stirred solution of 0.89 g (2.31 mmol) of triphenyltin chloride in 20 ml of THF. The resulting mixture was allowed to react for 36 h, the solvent was removed *in vacuo* (a reddish oil was obtained at this stage) and the residue was extracted with 40 ml of hexane. After concentrating the solution to approximately half the original volume and cooling to -10°C the red supernatant was transferred by cannulae into another three-neck flask, leaving behind most of the unreacted triphenyltin chloride. Subsequent crystallization of the supernatant at -10°C yielded less than 100 mg of 38, characterized by ^1H NMR spectroscopy and mass spectrometry. These spectroscopic techniques indicated the presence of 22a as well. From the NMR spectrum a 7:1 ratio of 38 to 22a could be deduced. Mass spectral data: dominant m/e values are observed at 828 (9.2%, M^+-2CO), 800 (66.7%, M^+-3CO), 528 (100.0%, $Ph_3GeC_7H_6FePh^+$), 451 (69.1%, $Ph_3GeC_7H_6Fe^+$), 395 (24.2%, $Ph_3GeC_7H_6{}^+$), [the most intense m/e-peak in each cluster is reported; 70 eV, 185°C].

The reaction of $[(Ph_3GeC_7H_6)Fe(CO)_3]^-$ with trimethylchlorosilane.

A solution of 36 in 40 ml of tetrhydrofuran, prepared from .65 g (1.22 mmol) 21c and .172 g (1.54 mmol) t-BuOK, was added dropwise to a magnetically stirred solution of trimethylchlorosilane (1.5 ml, 1.28 g) in 20 ml of tetrahydrofuran. The red solution of the dissolved anion immediately turned yellow upon contact with the Me_3SiCl solution. A pale yellow cloudy solution resulted upon completion of the addition. The mixture was stirred overnight, the solvent and excess trimethylchlorosilane (b.p. 57°C at 760 mm Hg) were removed *in vacuo* and 80 ml of hexane was added. Upon filtration, the solution was concentrated to about half the original volume. Cooling to -78°C produced a yellow oily solid identified as mostly 2. The supernatant was transferred to another three-neck flask and left to crystallize at -10°C. The limited amount of crystalline material so obtained was identified as the dimeric species 37. ^1H (100) NMR (31°C, $CDCl_3$, δ(ppm) downfield from internal TMS), 6.13 (H(5), 1H; $J_{4,5} \simeq 9$ Hz, $J_{5,7} \simeq 2$ Hz), 4.54 (H(2,3), 2H), 273 (H(1), 1H), 2.54 (H(4), 1H), 2.28 (H(7), 1H). The resonances were assigned on the basis of selective decoupling experiments. ^{13}C (22.6) NMR (30°C, benzene-d_6, δ(ppm) downfield from TMS), 34.4 (C(7)), 56.5 and 61.6 (C(1,4)), 88.2 and 93.4 (C(2,3)), 211.7 (CO); additional resonances were observed in the phenyl region at 129.0-140.5 (C(5,6) and C(phenyl)).

Preparation of the 3-Ph_3Ge and 6-Ph_3Ge isomers of $(Ph_3GeC_7H_6D)Fe(CO)_3$.

2.66 mmol of 36 in 30 ml of THF was carefully titrated with 8.3 ml of a 0.321 M solution of DCl in ether, to which 15 ml of THF was added. At the equivalence point the colour of the solution changed abruptly from red to yellow. The solution was stirred for another hour, THF removed *in vacuo* and 50 ml of hexane was added. The hexane solution was heated on a hot water bath (40-50°C), filtered *via* the cannulae technique[203] and left to crystallize at +4°C. The crystallization process was repeated until a complete separation of the 3- and 6-isomers was achieved. Three recrystallizations were sufficient. The composition of the crystals is best checked by ^1H FT NMR. A NMR spectrum of the initial crude solid showed the presence of both the 3- and 6-Ph_3Ge isomers in a 2 to 1 ratio. $(3\text{-}C_7H_6DGePh_3)Fe(CO)_3$ is the less soluble isomer. Anal. Calcd. for $C_{28}H_{21}O_3DGeFe$: C, 62.75; H, 4.32. Found: C, 62.77; H, 4.23 (3-isomer).

The reactions of 36 with HCl follow a pattern identical to that just described. No attempts were made to optimize the yields, which generally are only fair (~40-45%) due to the recrystallizations involved. It is noted however that very little $(C_7H_8)Fe(CO)_3$, which would result from the cleavage of the Ge-C bond, could be detected.

Reagents and Preparations, Chapter V.

Trifluoroacetic acid-d_1, 99% stated purity, was purchased from Merck Sharp & Dohme and purged with nitrogen before use.

Deuteration Reactions

All reactions of the triphenylgermyl substituted cycloheptatrienetricarbonyliron species with D^+ were performed in an identical fashion and the procedure is described here for the 3-Ph_3Ge isomer. Degassed TFA-d_1 (~.25 ml) was syringed into a cooled (-30°C) NMR which was equipped with a serum stopper and contained 50-75 mg of 39a dissolved in CD_2Cl_2/TMS (degassed; ~.3 ml/.05 ml). The solvents were then mixed by agitation and the spectra recorded at -25°C approximately 3 min after mixing.

Warming to ambient temperature did not affect the spectra.

Reagents and Preparations, Chapter VI.

Triphenylphosphine (Aldrich) and trimethylphosphite (Eastman) were used as received. 3-penten-2-one and trans-4-phenyl-3-buten-2-one were purchased from Aldrich and used without further purification. Dehydrated trimethylamine oxide was kindly supplied by Dr. A. Nakanishi. TCNE (Aldrich) was sublimed just prior to use. Carbon monoxide, 90% enriched in ^{13}CO, was purchased from Monsanto Research Corporation.

Preparation of (benzylideneacetone)tricarbonyliron.

11.36 g (78.0 mmol) of benzylideneacetone and 26.48 g (73.0 mmol) $Fe_2(CO)_9$ were heated in benzene (100 ml) under nitrogen with magnetic stirring for 6 h at 60°C. The subsequent work-up procedure is identical to that described by Lewis and co-workers.[201] At least two chromatographic separations on alumina(II) with benzene as eluent are required in order to obtain a pure, red solid material. The absence of impurities was ascertained by infrared and ^1H NMR spectra. ~~An~~ improved method has recently been described for the synthesis of (BDA)$Fe(CO)_3$ *via* the photochemical reaction of BDA with $Fe(CO)_5$.[198,199] The yield in the latter reaction is ~60% while the yield in the thermal reaction is less than 30%. ν_{CO} were observed at 2063(s), 2003(s), and 1980(s), the reported values are, 2065, 2005, and 1983.[201] The chemical shift values observed in the ^1H NMR spectra of (BDA)Fe(CO)$_3$ were identical to those reported by Lewis[201] and Brookhart.[198,199]

Preparation of (3-penten-2-one)Fe(CO)$_3$.

The procedure followed is similar to that outlined by Brookhart.[198] 6.0 g (72 mmol) of 3-penten-2-one and 21 g (106 mmol) of Fe(CO)$_5$ in 80 ml of benzene were photolyzed for 19 h with a 450-W Hanovia lamp. The solution was filtered to remove some brown precipitate and concentrated. 50 ml of hexane were added, resulting in the formation of more brown precipitate. The filtration was repeated at least two times and removal of hexane *in vacuo* then yielded the reddish brown (3-penten-2-one)Fe(CO)$_3$ as an oily residue, which was characterized by its ^1H NMR spectrum.[198]

The reaction of (η^4-7-Ph$_3$GeC$_7$H$_7$)Fe(CO)$_3$ with TCNE.

To a solution of TCNE (84.1 mg, .66 mmol) in 12 ml of CH_2Cl_2 was added a solution of 339.6 mg (.64 mmol) of 21c, also in 12 ml of CH_2Cl_2. After stirring the solution magnetically for 1.5 h a greenish, cloudy solution resulted. This solution was filtered and crystallization at low temperature was attempted but failed. Removal of the solvent and the addition of 30 ml of hexane resulted in a yellow solution from which only the starting materials could be recovered.

The reaction of (η^4-7-$Ph_3GeC_7H_7$)$Fe(CO)_3$ with trimethylamine oxide.

The procedure followed here was first developed by Dr. A. Nakanishi and Prof. J. Hooz of this department. 0.79 (1.31 mmol) of **21c** and 1.54 g anhydrous Me_3NO (~15 equivalents) were placed in a three-neck flask equipped with a reflux condenser and nitrogen inlet. 50 ml of THF was added to the reactants and the mixture was stirred magnetically for 2.5 h at ambient temperature. A yellow-brown precipitate formed. The mixture was then refluxed under nitrogen for 12 h at 53-55°C. After cooling the solution to ambient temperature, an infrared spectrum showed the absence of any carbonyl stretching frequencies and therewith indicates the completeness of the reaction. The solvent was removed *in vacuo*, hexane (90 ml) was added and the pale yellow solution filtered and concentrated. Cooling at 4°C produced pale yellow crystals (.2g, 48% yield) which were identified by NMR spectroscopy and mass spectrometry as bis(triphenylgermyl)ether, $Ph_3GeOGePh_3$.

The reaction of (η^4-7-$Ph_3GeC_7H_7$)$Fe(CO)_3$ with triphenylphosphine.

(η^4-7-$Ph_3GeC_7H_7$)$Fe(CO)_3$ (.419 g, 0.78 mmol) and Ph_3P (.500 g, 1.91 mmol) were dissolved in 40 ml of toluene and the reaction was monitored by infrared spectroscopy.

No reaction occurred at ambient temperature (48 h) or at 73°C (for 48 h also). After refluxing the mixture for 6 days at 114°C the starting iron complex was still the dominant species in solution. An intense absorption band at 1885 indicates the presence of $(Ph_3P)_2Fe(CO)_3$.[197] A single additional unassigned band is observed at 1919.

The reaction of $(\eta^3\text{-}C_7H_7)Fe(CO)_3SnPh_3$ with $Fe(CO)_5$.

$(\eta^3\text{-}C_7H_7)Fe(CO)_3SnPh_3$ (1.46 mmol, 0.847 g) and 26 ml (.193 mol) of iron pentacarbonyl in 110 ml of diethyl ether were irradiated for 7 h with a 450-W Hanovia high pressure mercury vapor lamp in an irradiation vessel equipped with a water-jacketed quartz immersion well. The mixture was filtered from $Fe_2(CO)_9$ and concentrated. After removal of all volatile components *in vacuo*, a reddish black solid remained. Addition of 50 ml of toluene resulted in a dark red solution (ν_{CO}, 2087.0(w), 2071.5(s), 2045.0(vs), 2011.5(s), 1990.0(m), and 1978.0(m) cm^{-1}) from which a red oil separated at -78°C. This oil was chromatographed on silica gel with benzene as eluent. The so obtained reddish solution exhibited ν_{CO} bands characteristic of $(C_7H_8)Fe(CO)_3$. No other products could be isolated or identified. Attempts to crystallize the above red oil were unsuccessful.

The reaction of (η^3-C_7H_7)Fe(CO)$_3$SnPh$_3$ with (BDA)Fe(CO)$_3$.

To a solution of 710 mg (1.22 mmol) of (η^3-C_7H_7)-Fe(CO)$_3$SnPh$_3$ in 50 ml of benzene was added a solution of 1.40 mmol of (BDA)Fe(CO)$_3$ in 30 ml of benzene. The progress of the reaction was followed by infrared spectroscopy. It was found to be necessary to reflux the solution for 90 h between 58°-64°C for the complete disappearance of absorption bands due to 22a to occur. Absorption bands due to the starting materials slowly disappeared and new ν_{CO} bands become apparent. After 90 h the solvent was removed *in vacuo*, leaving a red oil. Trituration of this oil with 100 ml of hexane resulted in the formation of a red solid (~.2 g) which was shown by infrared, ^1H and ^{13}C NMR spectroscopy and mass spectrometry to be a mixture of compounds. The solid was redissolved in 50 ml of toluene and to this solution was added 15 ml of pentane. Only a small amount of a brownish powder resulted and no crystalline sample could be obtained. Spectral characterization of the powder showed it to be identical in nature to the parent red solid above.

Anal: Calcd. for $C_{31}H_{22}O_6Fe_2Sn$: C, 51.67; H, 3.06.
Anal. Calcd. for $C_{30}H_{22}O_5Fe_2Sn$: C, 52.02; H, 3.18.
Found: C, 51.93 and 52.23; H, 3.24 and 3.27.

All attempts to recrystallize these solids did not lead to the separation of the components shown to be present in the mixture.

The reaction of $(\eta^3\text{-}C_7H_7)Fe(CO)_3SnPh_3$ with (3-penten-2-one)$Fe(CO)_3$.

A solution of 2.36 mmol (0.53 g) of the tricarbonyliron transfer reagent in 50 ml of benzene was added to a solution of 1.27 g (2.19 mmol) of 22a in 10 ml of benzene. Again the process of the reaction was followed by infrared spectroscopy. After 21 h at 70° the ν_{CO} bands due to the transfer reagent had disappeared. The solution was filtered and the benzene removed *in vacuo*, leaving a red oil. Addition of 100 ml of hexane produced a red solution and a yellow solid (~.150 g). An infrared spectrum of the red supernatant showed the presence of mainly the starting material $(\eta^3\text{-}C_7H_7)Fe(CO)_3SnPh_3$. The yellow powder was characterized by ^1H NMR spectroscopy, in CS_2, and the presence of two or three different species was deduced. The powder was recrystallized from CH_2Cl_2 and analytically pure crystals (~0.75 mg) of $(\eta^5\text{-}C_7H_7)Fe(CO)_3\text{-}SnPh_3$ were obtained.

Anal. Calcd. for $C_{27}H_{22}O_2FeSn$: C, 58.64; H, 4.01. Found: C, 58.48; H, 3.85.

The reaction of $(C_7H_7)Fe(CO)_3SnPh_3$ with ^{13}CO.

A ^{13}CO enriched sample of $(C_7H_7)Fe(CO)_3SnPh_3$ was prepared by dissolving 150 mg of the compound in 25 ml of hexane and irradiating the magnetically stirred solution for 6 h under 1 atmosphere of labelled carbon monoxide.

The extent of the enrichment (ca. 20%) was determined by mass spectrometry, 54 mg of material were recovered.

The reaction of $(\eta^3-C_7H_7)Fe(CO)_3SnPh_3$ with trimethylphosphite.

To a solution of 561 mg (.97 mmol) of 22a in 30 ml of benzene was added 164 mg (1.32 mmol) of $P(OMe)_3$. The resulting solution was photolyzed for 48 h. At this point no further changes in the infrared spectra were observed although ν_{CO} bands due to the starting complex were still present. Removal of the benzene *in vacuo*, addition of hexane and cooling at -78°C yielded an oily solid. Sublimation at 50°C onto a water-cooled probe gave a small amount of $Fe(CO)_3(P(OMe)_3)_2$, identified by its infrared spectrum.[197]

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